JOURNAL
OF
THE CHEMICAL SOCIETY.

ABSTRACTS OF PAPERS
ON
ORGANIC CHEMISTRY.

1911. Vol. C. Part I.

LONDON:
GURNEY & JACKSON, 10, PATERNOSTER ROW.
1911.

RICHARD CLAY & SONS, LIMITED,
BRUNSWICK STREET, STAMFORD STREET, S.E.,
AND BUNGAY, SUFFOLK.

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

Catalytic Reduction of Unsaturated Organic Compounds. Sergius Fokin (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 1071—1077).—In the hydrogenation of unsaturated compounds by hydrogen in the presence of metallic hydroxides, complex intermediate compounds are formed of the type $\begin{matrix} R^1{\cdot}CH{\cdot}CH{\cdot}R^2 \\ \diagdown\!\diagup \\ H_nM(OH)_m \end{matrix}$. These complex compounds yield colloidal solutions, and owing to their continuous formation and decomposition into $R^1CH_2{\cdot}CH_2R^2 + M(OH)_m$, they constitute the true carriers of the active hydrogen. Z. K.

The Systems Aluminium Bromide and Ethylene Dibromide. Boris N. Menschutkin (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 1308—1310).—Aluminium bromide dissolves readily in ethylene bromide, the saturated solution depositing small crystals. The solubility curve is characteristic for the case where the components form no chemical compound. The eutectic point lies at 2° at the approximate composition $AlBr_3,3{\cdot}37C_2H_4Br_2$. Z. K.

***n*-Butylhexylcarbinol.** Sergius Byrtschenko (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 876—879).—n-*Butylhexylcarbinol*, $C_{11}H_{24}O$, was obtained by Grignard's reaction by the action of magnesium

butyl iodide on heptaldehyde. It is a colourless liquid with an odour something like that of the juice of *Conium maculatum*. It has b. p. 223·5—225°/750·7 mm., 229·1—230·6° (corr.), D_0^0 0·8375, $D_0^{17·5}$ 0·8300, and solidifies at −3·5°. The *acetyl* derivative,

$$C_{13}H_{26}O_2,$$

b. p. 232·5—234°/747·7 mm., 239·3—240·8° (corr.), D_0^0 0·8677, $D_0^{17·5}$ 0·8562, has a faint pleasant odour, and solidifies at −1·5°. When oxidised with chromic mixture, the carbinol forms acids and *n-butyl hexyl ketone*, $C_{11}H_{22}O$, b. p. 218—221°/742 mm., 223·9—226·9° (corr.), D_0^0 0·8401, $D_0^{17·5}$ 0·8320, which is a liquid of pleasant odour and forms a *semicarbazone*, $C_{12}H_{25}ON_3$, m. p. 64·5°. Z. K.

Action of Magnesium Amalgam on Acetone. $\beta\gamma\epsilon$-Trimethylhexan-$\beta\gamma\epsilon$-triol and Some of its Derivatives. Louis Bouveault and René Locquin (*Ann. Chim. Phys.*, 1910, [viii], 21, 407—419, 425—432).—A more detailed account of the results published already by Richard and Langlais (Abstr., 1910, i, 455), with further particulars regarding the course of the reaction. The products resulting from the treatment of acetone with magnesium amalgam are of two kinds: (1) those derived from 2 mols. of acetone, namely, pinacone, mesityl oxide, β-methylpentan-β-ol-δ-one (see below), and the glycol corresponding with the last-mentioned alcohol; and (2) those derived from 3 mols. of acetone, namely, *iso*phorone and $\beta\gamma\epsilon$-trimethylhexan-$\beta\gamma\epsilon$-triol. Of these, the third appears to be the most important intermediate product, since from it pinacone, the chief final product, and mesityl oxide appear to be formed by decomposition in the course of the reaction (compare Couturier and Meunier, Abstr., 1902, i, 335; 1905, i, 326).

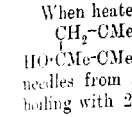
The dihydric alcohol, $C_6H_{14}O_2$, b. p. 102—103°/17 mm. or 188—190°/760 mm., previously referred to (Abstr., 1910, i, 456), furnishes a *diacetate*, b. p. 97—104°/17 mm., and when heated with pyruvic acid yields a *product*, $C_9H_{14}O_3$, m. p. 66°, b. p. 125—130°/17 mm., which crystallises in slender needles, and is provisionally regarded as a "dehydrated pyruvate." These reactions indicate that the dihydric alcohol is β-methylpentan-$\beta\delta$-diol, and this is confirmed by its preparation by the reduction of β-methylpentan-β-ol-δ-one,

$$HO\cdot CMe_2\cdot CH_2\cdot COMe$$

(Heintz, this Journ., 1876, i, 365), which also occurs in the products of the action of magnesium amalgam on acetone; it has b. p. 75—80°/17 mm., and is readily decomposed on heating, especially in presence of an alkali. Dilute sulphuric acid converts it into mesityl oxide.

$\beta\gamma\epsilon$-Trimethylhexan-$\beta\gamma\epsilon$-triol, $OH\cdot CMe_2\cdot CMe(OH)\cdot CH_2\cdot CMe_2\cdot OH$, already described (succeeding abstract, and Abstr., 1910, i, 456), is dealt with in detail in the second paper. On treatment with chromic acid, it is decomposed, yielding 1 mol. each of acetone and β-methylpentan-β-ol-δ-one (see above). When heated alone or with acids, the trihydric alcohol undergoes dehydration, and in the case of acetic anhydride or pyruvic acid furnishes an ester of the dehydrated product.

When heated alone, the alcohol loses $1H_2O$, giving a *substance* (*a*), $CH_2\text{-}CMe_2$>O, m. p. 77°, b. p. 75°/10 mm., which crystallises in $HO\cdot CMe\text{-}CMe_2$
needles from a mixture of light petroleum and ether, and this on boiling with 20% sulphuric acid is transformed into a *cyclic oxide* (*b*) (annexed formula), b. p. 126—127°, D^{25} 0·826, a mobile oil having a terpene-like odour. Both these products are formed when the trihydric alcohol is boiled with 20% hydrochloric acid, and (*b*) almost entirely when 20% sulphuric acid is used, although in this case a minute amount of an *isomeride* (*b'*) of (*a*) is produced. This has b. p. 168°/760 mm. With a boiling saturated solution of oxalic acid, substance (*a*) only is formed. Boiling acetic anhydride converts the trihydric alcohol into a *dehydrated monoacetate*, $C_{11}H_{20}O_3$, b. p. 89°/17 mm., D_4° 0·989, which appears to be the acetyl derivative of substance (*a*), since it is also formed by the acetylation of the latter.



Pyruvic acid heated with the alcohol yields a substance (*b*) in small quantity, and in addition a *dehydrated pyruvate*, $C_{12}H_{18}O_3$, m. p. 122°, b. p. 140°/13 mm., which crystallises in needles, and is probably the pyruvate of substance (*a*), since it is also produced from this by the action of pyruvic acid. T. A. H.

Synthesis of $\beta\zeta$-Dimethylheptan-$\beta\delta\zeta$ triol and of $\beta\gamma\epsilon$-Trimethylhexan-$\beta\gamma\epsilon$-triol. II. Louis Bouveault and Ferdinand Levallois (*Ann. Chim. Phys.*, 1910, [viii], 21, 419—425).—This work was undertaken with a view to the determination of the constitution of the trihydric alcohol obtained by the action of magnesium amalgam on acetone (preceding abstract, and Richard and Langlais, Abstr., 1910, i, 455), which was at one time thought to be the first, but is now known to be the second, of the two substances synthesised.

$\beta\zeta$-Dimethylheptan-$\beta\delta\zeta$-triol,

$$OH\cdot CMe_2\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot CMe_2\cdot OH,$$

m. p. 54°, b. p. 155—160°/18 mm., obtained by the interaction of magnesium methyl iodide with methyl β-hydroxyglutarate, is a colourless liquid of sweet taste, and somewhat resembles glycerol.

Methyl citramalate (α-methylmalate), which was used as the starting point for the preparation of the trihydric alcohol, is not easily obtained in good yield by Michael's process (Abstr., 1893, i, 146). For its preparation, ethyl acetoacetate was treated with anhydrous hydrogen cyanide in presence of triethylamine, and the resulting *nitrile*,

$$OH\cdot CMe(CN)\cdot CH_2\cdot CO_2Et,$$

b. p. 133°/20 mm., saturated with dry hydrogen chloride in presence of excess of methyl alcohol, and the resulting imino-ether hydrochloride poured on ice, treated with potassium carbonate, and the methyl citramalate, b. p. 112°/15 mm., extracted with ether and purified by distillation. With magnesium methyl iodide, it furnished $\beta\gamma\epsilon$-trimethylhexan-$\beta\gamma\epsilon$-triol, $OH\cdot CMe_2\cdot CMe(OH)\cdot CH_2\cdot CMe_2\cdot OH$, identical with that described already (preceding abstract, and Richard and Langlais, Abstr., 1910, i, 455). T. A. H.

Aliphatic Nitro-compounds. VIII. α-Nitropropionic Acid. WILHELM STEINKOPF and ALEXANDER SUPAN (*Ber.*, 1910, 43, 3239—3249. Compare Abstr., 1909, i, 559, 874).—Ethyl α-nitropropionate can be prepared by the action of concentrated alcoholic ammonia on ethyl nitro*iso*succinate; the first product is the ammonium salt of the *aci*-nitro-ester, m. p. 119° (decomp.), but this reacts with dilute sulphuric acid, yielding the free ester.

Ethyl nitro*iso*succinate is best prepared by nitrating ethyl *iso*succinate with a mixture of fuming nitric acid and acetic anhydride (compare Bouveault and Wahl, Abstr., 1904, i, 795). It has b. p. 121—122°/11 mm., whereas Salway gives 108°/13 mm., and Ley and Hantzsch give 126—127°/10 mm. The yields obtained by methylating ethyl nitromalonate by Ulpiani's method (Abstr., 1903, i, 791) or by Purdie's method (Trans., 1899, **75**, 157) are poor.

The *ammonium* salt of α-nitropropionamide, $C_3H_9O_3N_3$, formed by heating ethyl α-nitropropionate with concentrated alcoholic ammonia for two hours at 100°, crystallises from a mixture of alcohol and ether, and has m. p. 127—128°. The *amide*, $NO_2{\cdot}CHMe{\cdot}CO{\cdot}NH_2$, is best prepared by converting the ammonium salt into the insoluble lead salt, suspending this in dry ether, and passing in dry hydrogen sulphide at 0°. It crystallises from chloroform or ether in slender, colourless needles, m. p. 68—69°. Chlorine reacts with an ice-cold aqueous solution of the ammonium salt, yielding *α-chloro-α-nitropropionamide*, $NO_2{\cdot}CClMe{\cdot}CO{\cdot}NH_2$, which crystallises from water in glistening, colourless plates, m. p. 82°. The corresponding *bromo*-derivative, $C_3H_5O_3N_2Br$, has m. p. 89°. The *dipotassium* salt of α-nitropropionic acid, $C_3H_3O_4NK_2,EtOH$, is obtained as long needles when the ammonium salt of ethyl *aci*nitropropionate is boiled for fifteen minutes with an alcoholic solution of potassium hydroxide (20%). The corresponding *sodium* salt, $C_3H_3O_4NNa_2$, separates from a mixture of alcohol and water in long needles.

α-Nitropropionic acid, $NO_2{\cdot}CHMe{\cdot}CO_2H$, is obtained by suspending the silver salt in a small amount of water, and adding the theoretical amount of *N*-hydrochloric acid and extracting rapidly with ether, or by mixing a concentrated aqueous solution of the sodium salt with much ether, cooling in a freezing mixture, and shaking whilst the theoretical amount of *N*-hydrochloric acid is added. The ethereal solution is dried with phosphoric oxide and the ether removed. It crystallises from carbon disulphide in long, colourless needles, m. p. 61—61·5° (decomp.).

Nitroacetaldehydephenylhydrazone is formed by the action of an aqueous solution of benzenediazonium chloride on a not too dilute solution of sodium α-nitropropionate. It crystallises from alcohol in golden-yellow plates, m. p. 136·5°.

Nitroacetic acid can be obtained from its potassium salt in much the same manner as the nitropropionic acid from its sodium salt.

The conversion of ethyl nitro*iso*succinate into ethyl nitropropionate and then into nitropropionamide by means of ammonia supports Ratz's view regarding the mechanism of the reaction between ethyl nitromalonate and ammonia (compare Abstr., 1904, i, 857). J. J. S.

Ammonium Salts of Fatty Acids (Oleic, Palmitic, Stearic), and the Separation of the Saturated Fatty Acids (Palmitic and Stearic) from Oleic Acid. I. PIETRO FALCIOLA (*Gazzetta*, 1910, **40**, ii, 217—229).—The author has studied the composition and the solubilities (in some cases quantitatively) of the ammonium salts of the fatty acids mentioned, and has found that the oleate is soluble in cold alcohol, whilst the palmitate and stearate are not. The quantitative separation is effected by dissolving the mixture of acids in warm ether, passing ammonia through the solution, and allowing it to cool to the ordinary temperature. When almost all the ether has evaporated, the pasty residue is extracted with cold ammoniacal alcohol (at about 0°), filtered at the pump, and washed with a further portion of this solvent. From precipitate and filtrate the separated free fatty acids can be liberated by treatment with dilute hydrochloric acid. The methods gives results sufficiently accurate for technical analysis.

When concentrated aqueous ammonia is added to a warm alcoholic solution of stearic acid, *ammonium stearate*, $C_{18}H_{35}O_2{\cdot}NH_4$, separates as a crystalline precipitate on cooling. When heated, it undergoes change at 90°, and is completely melted at about 110° (with evolution of gas). It loses ammonia on keeping, and, after treatment with water, the crystals have the composition of the *acid* salt,

$$C_{18}H_{36}O_2,C_{18}H_{35}O_2{\cdot}NH_4.$$

The *palmitate*, $C_{16}H_{31}O_2{\cdot}NH_4$, is similarly prepared, and has similar properties. It softens towards 90°, and melts completely above 100° (with evolution of gas). Treatment with water converts it into the *acid* salt, $C_{16}H_{32}O_2,C_{16}H_{31}O_2{\cdot}NH_4$. The *oleate*, $C_{18}H_{33}O_2{\cdot}NH_4$, is prepared by passing ammonia into an ethereal solution of oleic acid. It loses ammonia when kept in the air. With water, it yields a gelatinous colloidal solution. R. V. S.

The Elaidin Reaction. SERGIUS FOKIN (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1068—1073).—From theoretical reasoning it seems probable that the elaidin reaction given with oleic acid by sulphurous and nitrous acids would also be given by many other substances, capable like these of internal re-grouping and existence in at least two forms of different configuration. Phosphoric and phosphorous acids both give the elaidin reaction with oleic acid when heated at 170—180° in a slow current of hydrogen and then in a sealed tube, the former acid reacting more rapidly than the latter. In the presence of phosphorus trichloride, the reaction is still slower.

Tetranitromethane and ethyl nitrite both convert oleic acid into elaidic acid, an additive compound of the nitromethane and unsaturated acid being formed, and gases also evolved in the former case. Elaidic acid when heated with phosphoric acid for thirty to forty hours at 180°, yields an oleic acid, which does not react with ethyl nitrite, is more stable than elaidic or ordinary oleic acid, and seems to be identical with the oleic acid obtained by the prolonged action of sunlight on the ordinary acid. Z. K.

The Optical Behaviour of Lactic Acid in a Meat Preparation. Ernst Salkowski (*Zeitsch. physiol. Chem.*, 1910, 69, 471—473).—In an American meat-juice it was noticed that in time the sarcolactic acid passes more and more into an inactive modification of the acid. In the course of a year the change was almost complete. It is suggested that the cause is the presence of a large amount of potassium dihydrogen phosphate. W. D. H.

New Method for Preparation of Glycidic Esters. Georges Darzens (*Compt. rend.*, 1910, 151, 883—884).—Ethyl α-chloro-β-hydroxy*iso*valerate is conveniently prepared by adding magnesium amalgam to a mixture in molecular proportions of acetone and ethyl dichloroacetate dissolved in benzene, the product being then treated with water. Esters of this type are readily converted into the corresponding glycidic esters; thus, on treating the foregoing compound with sodium ethoxide, a theoretical yield of ethyl ββ-dimethylglycidate is obtained. Although the condensation of ethyl dichloroacetate with ketones other than acetone has not been successful, yet this method of synthesising glycidic esters appears to be general, inasmuch as the required hydroxy-ester can always be obtained through the action of hypochlorous acid on the corresponding unsaturated acid. W. O. W.

Pinacolin Derivatives. A. Richard (*Ann. Chim. Phys.*, 1910, [viii], 21, 323—406. Compare Abstr., 1910, i, 455, 458, 462).—This work was undertaken in order to ascertain what influence the ψ-butyl group has on the stability of the compounds in which it occurs, and particularly whether the unsymmetrical character of substances containing this group gives rise to any peculiar form of isomerism. The results obtained show that the alkyl chlorides containing this group allow of ready molecular transformation when they contain a hydrogen atom attached to the carbon, which carries the chlorine atom, but in no case was any isomerism noticed among the acids containing this group.

Methyl pivalate has D_4^0 0·891. The ethyl ester has D_4^0 0·875, and on reduction by Bouveault and Blanc's method (Abstr., 1903, i, 557) furnishes ββ-dimethylpropyl alcohol, $CMe_3·CH_2·OH$ (Tissier, Abstr., 1893, i, 542), m. p. 50°, b. p. 113—115°/760 mm. or 64°/100 mm., which yields a *phenylurethane*, m. p. 114°, and a *pyruvate*, b. p. 78—80°/23 mm., the *semicarbazone* of which is crystalline and melts at 166°. On saturation with dry hydrogen chloride, the alcohol yields the corresponding chloride, b. p. 87—90°, but this dissociates when heated into β-methyl-Δ^α-butylene and hydrogen chloride, and the former, when re-combined with hydrogen chloride and then transformed into the acetate and the latter hydrolysed, yields the isomeric *tert.* alcohol, $CMe_2(OH)·CH_2Me$ (compare Tissier, *loc. cit.*). Magnesium ββ-dimethylpropyl chloride on treatment with oxygen furnishes an *alcohol*, m. p. −12°, b. p. 101—103°, D_4^0 0·827, possessing a camphoraceous odour, which on heating with pyruvic acid is not esterified, but is dehydrated, yielding β-methyl-Δ^β-butylene. Bouveault has shown that this reaction is characteristic of tertiary alcohols (Abstr.,

1904, i, 465). With phenylcarbimide, dehydration also occurs. With carbon dioxide, magnesium $\beta\beta$-dimethylpropyl chloride gives rise to $\beta\beta$-dimethylbutyric acid.

Pinacolin may be reduced by sodium in alcohol, potassium hydroxide in alcohol, or sodium in moist ether, giving in all cases good yields of pinacolyl alcohol (compare Friedel and Silva, this Journ., 1873, 26, 488). The latter furnishes a *pyruvate*, b. p. 78—80°/17 mm., and the *semicarbazone* of this is crystalline and melts at 175°. The magnesium derivative of the chloride of this alcohol on treatment with oxygen yields dimethyl*iso*propylcarbinol, which confirms Couturier's observation that the chloride is unstable and on heating yields $\beta\gamma$-dimethyl-Δ^{β}-butylene. The present transformation may be represented thus:

$$CMe_3\cdot CMeHCl \longrightarrow CMe_2{:}CMe_2 \longrightarrow CMe_2Cl\cdot CHMe_2 \longrightarrow OH\cdot CMe_2\cdot CHMe_2.$$

With carbon dioxide, magnesium pinacolyl chloride furnishes *aaβ-trimethylbutyric acid*, m. p. 50°, b. p. 106°/15 mm.

aaββ-Tetramethylpropyl chloride (Henry, Abstr., 1906, i, 477) reacts with magnesium methyl iodide, forming a product which on treatment with carbon dioxide gives $\beta\beta\gamma\gamma$-tetramethylbutane (*loc. cit.*, p. 173) and *aaββ*-tetramethylbutyric acid, $CMe_3\cdot CMe_2\cdot CO_2H$. This chloride is therefore much less liable to undergo intramolecular transformation than those described above, due to the fact that it contains no free hydrogen atom associated with the carbon carrying the chlorine atom.

Trimethylpyruvic acid, $CMe_3\cdot CO\cdot CO_2H$, prepared by Glücksmann's method (Abstr., 1890, i, 237), crystallises in the absence of moisture, and then melts at 125°. In moist air it absorbs $\frac{1}{2}H_2O$, and then has m. p. 90°. The *oxime*, m. p. 85°, crystallises in colourless spangles; the *hydrazone*, $N_2\left(:C<\begin{matrix}CMe_3\\CO_2H\end{matrix}\right)_2$, m. p. 207°, forms sulphur-yellow needles, and the *semicarbazone* has m. p. 195° (decomp.). The *methyl* ester, b. p. 69—70°/20 mm. or 160—162°/760 mm., D_4^0 0·934, is a colourless, mobile oil, and furnishes a *semicarbazone*, m. p. 125°, and an *oxime*, m. p. 66°, b. p. 125°/20 mm. The *ethyl* ester, b. p. 76—77°/20 mm., yields a *semicarbazone*, m. p. 115°, and an *oxime*, m. p. 22—23°, b. p. 131—133°/20 mm., which reacts with phenylcarbimide to give a *phenylurethane*, m. p. 123—124°, crystallising in long, brilliant needles. On reduction, the oxime yields *ethyl a-amino-ββ dimethylbutyrate*, $CMe_3\cdot CH(NH_2)\cdot CO_2Et$, b. p. 85°/15 mm., D_4^0 0·952, which with phenylcarbimide yields the corresponding *phenylcarbamide*, m. p. 78°, with benzoyl chloride gives *ethyl ψ-butylhippurate*, m. p. 64°, b. p. 198—200°/15 mm., and also yields a *picrate*, m. p. 134°.

Trimethylpyruvic acid condenses with aniline to form a product which, on distillation, yields aa-dimethylpropaldehyde (compare Bouveault, Abstr., 1896, i, 649) and some *ββ-dimethylpropylideneanil*ine, $CMe_3\cdot CH{:}NPh$, b. p. 101—102°/20 mm., D_4^0 0·941. aa Dimethylbutaldehyde yields an *oxime*, m. p. 41°, b. p. 65°/20 mm., and an *azine*, m. p. 79°. Ethyl trimethylpyruvate combines with anhydrous hydrogen cyanide in presence of trimethylamine, forming the cyanohydrin (Carlinfanti, Abstr., 1899, i, 671), and this, on hydrolysis with sulphuric acid at −15°, is converted into the *amide*

of ethyl ψ butyltartronate, $CMe_3 \cdot C(OH)(CO \cdot NH_2) \cdot CO_2Et$, m. p. 66°, b. p. 162—164°/15 mm. With ammonia in alcohol, ethyl trimethylpyruvate forms a *substance,* $C_{12}H_{21}O_2N_3$, m. p. 225°, which is crystalline.

When methyl or ethyl trimethylpyruvate is treated with magnesium methyl iodide or magnesium methyl bromide, α-hydroxy-αββ-trimethylbutyric acid or its ester is formed, with a small amount of the aldehyde corresponding with this acid. Pinacolin combines with hydrogen cyanide to form α-hydroxy-αββ-trimethylbutyronitrile (Carlinfanti, Abstr., 1898, i, 234), m. p. 113°, b. p. 90°/12 mm., and this on treatment with sulphuric acid at 0° is hydrolysed to the *amide,* m. p. 140—141°, b. p. 170°/10 mm. (decomp.), which is converted by boiling with hydrochloric acid into *α-hydroxy-αββ-trimethylbutyric acid,* $CMe_3 \cdot CMe(OH) \cdot CO_2H$, m. p. 141°, b. p. 130°/14 mm. The *methyl* ester, b. p. 65·5°/12 mm., D_4^0 1·002, and the *ethyl* ester, b. p. 74°/12 mm., D_4^0 0·975, are oils, the latter having a camphoraceous odour. The acid condenses with chloral to form a *chloralide,* m. p. 85°, b. p. 126—127°/14 mm.

When methyl hydroxytrimethylbutyrate is treated with magnesium methyl iodide, it yields (1) *α-hydroxy-αββ-trimethylbutaldehyde,* b. p. 82—84°/16 mm., which gives an *oxime,* m. p. 65°, b. p. 126—127°/15 mm., that regenerates the nitrile on treatment with acetic anhydride, and (2) *ββγδ-tetramethylamylene βγ-glycol,* $HO \cdot CMe_2 \cdot CMe(OH) \cdot CMe_2$ m. p. 22°, b. p. 96—98°/16 mm., and this, when boiled with 20% sulphuric acid, furnishes the hexamethylacetone described by Haller and Bauer (Abstr., 1910, i, 219).

α-Hydroxy-ββ-dimethylbutyric acid yields a *chloralide,* m. p. 83°, b. p. 130°/15 mm., and, when heated at 240°, gives αα-dimethylpropaldehyde (see above) and a less volatile material, which, on distillation under reduced pressure, furnishes (1) *trimeric αα-dimethylpropaldehyde,* b. p. 104—105°/18 mm., D_4^0 0·979, and (2) the *dilactide* of *α-hydroxy ββ-dimethylbutyric acid,* m. p. 84°, b. p. 148°/13 mm., a substance crystallising in brilliant spangles. αα-Dimethylpropaldehyde combines with hydrogen cyanide in presence of pyridine, forming *α-hydroxy-ββ-dimethylbutyronitrile,* b. p. 100°/100 mm., D_4^0 0·911, and this, on hydrolysis by sulphuric acid at 0°, gives the corresponding *amide,* m. p. 135°, which, when boiled with hydrochloric acid, furnishes the corresponding acid; the *methyl* ester of the latter has b. p. 69—70/16 mm., D_4^0 1·044, and the *ethyl* ester has b. p. 79—80°/16 mm. and D_4^0 0·987. The acid, on treatment with phosphorus pentachloride, followed by methyl alcohol, furnishes (1) a *liquid,* $C_9H_{19}O_6P$, b. p. 165—170°/23 mm., D_4^0 1·437, which is neutral to litmus, and possesses an alliaceous odour; (2) dimethyl hydrogen phosphate; (3) methyl hydroxydimethylbutyrate; (4) an *acid,* b. p. 75—90°/22 mm., and (5) a second *acid,* b. p. 150—155°/22 mm. The first substance probably has the constitution

$$PO(OMe)_2 \cdot O \cdot CH(CMe_2) \cdot CO_2Me.$$

Under like conditions with phosphorus pentabromide, a neutral substance, $C_7H_{13}O_2Br$, b. p. 115—125°/23 mm., is formed. Phosphorus tribromide reacts with ethyl hydroxydimethylbutyrate to give two products, *one* having b. p. 85—90°/20 mm., and the *other,*

190—215°/20 mm. With phosphorus tri-iodide the methyl ester yields an *iodo*-compound, having b. p. 102—105°/18 mm., and a *substance*, b. p. 200°/18 mm. (approx.), which contains phosphorus.

T. A. H.

The Photo-chemical Inversion of Maleic Acid. LUDWIK BRUNER and M. KRÓLIKOWSKI (*Bull. Acad. Sci. Cracow*, 1910, 192—208).—As a preliminary step in the investigation of the photo-chemical transformation of maleic into fumaric acid in presence of a small quantity of bromine, the authors have measured the rates at which the two acids take up bromine with the formation of dibromosuccinic acid. The experiments were made in dilute aqueous solution at 25° in the dark, the reacting substances being present in equimolar proportions. The values obtained for the velocity constant, on the assumption that the reaction is bimolecular, decrease as the reaction proceeds, and this is found to be due to the increasing acidity of the solution as a consequence of the formation of bromomalic acid and hydrobromic acid by hydrolysis of the dibromosuccinic acid formed in the primary reaction. In support of this view, it is found that the addition of mineral acids diminishes the rate of the reaction, but if these are present in considerable excess, the progress of the reaction is in agreement with the equation for a bimolecular change. Under these conditions it is found that the rate at which bromine is taken up by maleic acid is fifteen times as great as for fumaric acid.

In connexion with the photo-chemical inversion, two methods have been worked out for the quantitative estimation of fumaric and maleic acids in their mixed solutions. These depend respectively on measurements of the electrical conductivity and of the solubility of fumaric acid in the solutions.

The rate of transformation of maleic acid into fumaric in presence of a trace of bromine and in sunlight shows that the reaction is unimolecular. If the light is removed whilst the reaction is in progress, the inversion process ceases, and there appears to be no after effect. The active rays are those at the blue end of the spectrum, the reaction ceasing when a 2 cm. layer of 7·5% potassium dichromate or of 5% bromine solution is interposed.

Between 16° and 32° the velocity of the inversion is practically independent of the temperature. The proportion of maleic acid, which is transformed when the reaction comes to an end, increases with the amount of bromine present in the solution. For small concentrations of bromine, the percentage of fumaric acid in the equilibrium mixture is approximately proportional to the quantity of bromine present.

For a definite amount of bromine the proportion of fumaric acid in the final mixture diminishes as the concentration of the maleic acid increases. If fumaric acid is added to the original solution, the proportion of maleic acid which is inverted diminishes. On the other hand, addition of other acids, such as nitric and sulphuric acids, increases the proportion of the maleic acid which is finally transformed.

H. M. D.

Action of Zinc and Magnesium Organic Compounds on Ortho-formic Ester. M. L. SHDANOVITSCH (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1279—1297).—When zinc reacts on a mixture of ethyl orthoformate and ethyl α-bromo*iso*butyrate in the absence of any solvent, the following products are obtained: (1) *Ethyl ββ-diethoxy-αα-dimethylpropionate*, $CH(OEt)_2 \cdot CMe_2 \cdot CO_2Et$, b. p. 211—212° (748·2 mm., D^{19}_{4} 0·9520, n_{18} 1·41886, which when heated with nitric acid readily yields dimethylmalonic acid, m. p. 184—185·5° (decomp.); (2) Ethyl tetramethylacetoacetate, $CHMe_2 \cdot CO \cdot CMe_2 \cdot CO_2Et$, which when hydrolysed with hydrochloric acid yields di*iso*propyl ketone, the semicarbazone of which has m. p. 153—154·5° (Blaise gives 150—151°). (3) *Ethyl γ-keto-ααββδδ-hexamethyladipate*,

$$CO_2Et \cdot CMe_2 \cdot CMe_2 \cdot CO \cdot CMe_2 \cdot CO_2Et,$$

b. p. 303—309°/760 mm. (4) An *unsaturated keto*-ester, probably $CH_2{:}CMe \cdot CO \cdot CMe_2 \cdot CO_2Et$, which on hydrolysis yields methacrylic acid, $CH_2{:}CMe \cdot CO_2H$, of which the silver salt was analysed. (5) The resinous product obtained after the distillation of the crude product yields, on hydrolysis, a quantity of cubic crystals, possibly tetramethylsuccinic acid. The *silver* salt, $C_{13}H_{19}O_6Ag_3$ or $C_8H_{12}O_4Ag_2$, was analysed; some butaldehydes were also found amongst the products. When magnesium is substituted for zinc, the chief products of the reaction are: (1) ethyl tetramethylacetoacetate; (2) *ethyl β-keto-δδ-diethoxy-ααγγ-tetramethylvalerate*,

$$CH(OEt)_2 \cdot CMe_2 \cdot CO \cdot CMe_2 \cdot CO_2Et,$$

b. p. 160—161°/23 mm., 272—273°/760 mm., a yellow liquid with a pleasant sweet odour; (3) ethyl β-hydroxytetramethylglutarate,

$$CO_2Et \cdot CMe_2 \cdot CH(OH) \cdot CMe_2 \cdot CO_2Et,$$

which is separated from the acetal with great difficulty. Z. K.

Cholic Acid. II. MARTIN SCHENCK (*Zeitsch. physiol. Chem.*, 1910, **69**, 383—389).—Reductodehydrocholic acid (Abstr., 1910, i, 10) is now found to have m. p. 190—192° (not sharp), and is dextrorotatory, $[\alpha]_D = +29°$, when dissolved in alcohol. It appears to be identical with the acid obtained by Hammarsten by reducing dehydrocholic acid with sodium amalgam.

A modified method is given for obtaining cholic acid from ox gall and for preparing some of its known derivatives; for this the original paper must be consulted. An examination of cholanic acid, $C_{24}H_{38}O_2$, showed that six of the oxygen atoms are in three carboxyl groups, while the seventh is in a keto-group. The author has succeeded in preparing an oxime, $C_{24}H_{39}O_2{:}N \cdot OH$, crystallising in plates or needles from acetone, which begins to decompose at 160°, and is completely decomposed at 197°. E. J. R.

Complex Derivatives of Molybdic Acid. ARRIGO MAZZUCCHELLI (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 439—445. Compare Abstr., 1910, i, 657, 708).—Determinations of the rotatory power of solutions of tartaric acid and molybdates are complicated by the variations in the acidity and ionisation with the composition of the solution, and it is preferable to examine solutions containing only tartaric and molybdic acids. The addition of other acids to such a solution lowers the

rotatory power, hydrochloric acid having a greater effect than acetic, and the rotatory power tends to a limit when the quantity of hydrochloric acid is increased. The conclusion is drawn that the exaltation observed on adding further quantities of molybdic acid to molybdotartaric acid is specific, and is due to the formation of complexes. Cryoscopic determinations show that the group $C_4H_4O_6,MoO_3$ is largely polymerised in solution. On the other hand, sodium molybdo-oxalate has a normal molecular weight. C. H. D.

Complexes of Permolybdic and Pertungstic Acids with Active Organic Acids. Arrigo Mazzucchelli and Mario Borghi (*Gazzetta*, 1910, 40, ii, 241—261).—The rotatory power of the *ammonium molybdotartrate*, $(NH_4)_2C_4H_4O_6,MoO_3$, at different concentrations agrees fairly well with those observed by Rosenheim and Itzig (Abstr., 1900, i, 135, 272) for the potassium and sodium salts of this composition, so that it may be considered to produce the same active ion. To solutions of this salt containing in combination 1·016% of tartaric acid (by volume), hydrogen peroxide was added in the quantity required by the ratio $MoO_3 : 2H_2O_2$. The specific rotatory power of the tartaric acid is thereby reduced from +528° to +203°. It rises again when the solution is kept, owing to catalytic decomposition of the hydrogen peroxide, and if this decomposition is accelerated by the addition of amyl alcohol (compare Brode, Abstr., 1901, ii, 433) the specific rotatory power reaches its initial value in the course of some hours. The change of specific rotatory power caused by hydrogen peroxide is not due to scission of the molybdotartaric ion into ozomolybdate and tartaric acid, because when more hydrogen peroxide is added, making the ratio $MoO_3 : 3H_2O_2$, no further change in rotatory power occurs. The specific rotatory power in a solution containing hydrogen peroxide in the ratio $MoO_3 : 3H_2O_2$ diminishes on dilution.

The authors have made experiments to ascertain whether complex ozo-salts exist corresponding with the molybdotartrates containing other numbers of molybdenum trioxide groups, the method adopted being to mix hydrogen peroxide with solutions of tartaric acid and of the yellow acid, $MoO_3,2H_2O$ (compare Rosenheim, Abstr., 1906, ii, 762). The rotatory power attains a maximum when the solution contains $C_4H_4O_6,4MoO_3,4H_2O_2$, so that the existence of a complex of this composition is probable, although for other reasons not certain.

Rosenheim has shown (Abstr., 1904, ii, 128) that white molybdic acid, MoO_3,H_2O, differs from the yellow dehydrated acid, $MoO_3,2H_2O$, even in solution. White α-molybdic acid is readily obtained by treating methyl molybdate with water. Its behaviour with tartaric acid and hydrogen peroxide is analogous to that of the yellow acid, but the rotatory powers of solutions of the same composition are different, and the maximum corresponds with the existence of a compound $C_4H_4O_6,5(MoO_3,H_2O_2)$, thus affording a further proof of the difference between the two acids.

Solutions of sodium molybdomalate, obtained by mixing equimolecular quantities of sodium molybdate and malic acid, containing 1 mol. of hydrogen peroxide, rapidly decompose, and the specific rotatory power of the malic acid returns to the value +151° due to the molybdo-

malate. When an excess of hydrogen peroxide is taken, the specific rotation at first is about $-140°$, but eventually it becomes $+15°$. It is considered that the hydrogen peroxide in the undecomposed solution forms the complex $Na_2C_4H_4O_5,MoO_4$.

Similar experiments with solutions of sodium tungstotartrate, $Na_2C_4H_4O_6.WO_3$, indicate the formation of a complete oxotungstotartrate, which contains probably equimolecular quantities of tungsten trioxide and hydrogen peroxide (compare Mazzucchelli and Inghilleri, Abstr., 1908, i, 755). The rotatory power does not alter when the solution is kept, so that the decomposition of the hydrogen peroxide is slower in presence of tungsten trioxide than in the presence of molybdenum trioxide (compare Brode, *loc. cit.*). R. V. S.

Resolution of Pentane-$\beta\beta\delta$-tricarboxylic Acid and of *s*-Dimethylglutaric Acid into Optically Active Components. Elof Möller (*Ber.*, 1910, 43, 3250—3251). — Pentane-$\beta\beta\delta$-tricarboxylic acid, $CMe(CO_2H)_2{\cdot}CH_2{\cdot}CHMe{\cdot}CO_2H$, obtained by condensing ethyl *a*-bromo*iso*butyrate with the sodio-derivative of ethyl *iso*succinate and hydrolysing the resulting ester, separates from water in slender crystals, and has $K = 0{\cdot}220$ at 25°. The *potassium* salt, $C_8H_{11}O_6K$, forms readily soluble prisms, and the *normal* salt, $C_8H_9O_6K_3,H_2O$, transparent, deliquescent crystals. It can be resolved by means of strychnine; the salt of the *d*-acid is sparingly soluble, and crystallises in long, pointed needles, whereas the salt of the *l*-acid forms long, transparent prisms. The *d*-acid has $[\alpha]_D^{20}$ +16·3°, and the *l*-acid $[\alpha]_D^{20}$ −15·6°, in aqueous solution. The *d*-acid evolves carbon dioxide at 140°, and yields a dimethylglutaric acid with $[\alpha]_D^{20}$ +16·2°; the *l* acid under similar conditions yields a dibasic acid with $[\alpha]_D^{20}$ −15·7°. The inactive acid evolves carbon dioxide at 135°, and at 140° yields a mixture of the two *s*-dimethylglutaric acids. These can be separated by means of their calcium hydrogen salts, and the acid with m. p. 140—141° can be resolved by means of strychnine into its active constituents. The salt of the *d*-acid crystallises, first, in large prisms, and then the salt of the *l*-acid in small, felted needles.

The *d*-acid has $[\alpha]_D^{20}$ +41·9°, and the *l*-acid, $[\alpha]_D^{20}$ −24·3°. The acid melting at 141° is thus the racemic form, and the acid with m. p. 128° the meso-form. J. J. S.

Glucodeconic Acids. L. H. Philippe (*Compt. rend.*, 1910, 151, 986—988).—The preparation of *a*-glucodeconic acid, $C_{10}H_{20}O_{11}$, from gluconose by Fischer's method is described. The acid could not be isolated in a pure state, since on concentrating its aqueous solutions, crystals were deposited consisting of an hydrated *lactone*,

$$C_{10}H_{18}O_{10},H_2O,$$

m. p. 168° (anhydrous, m. p. 214°), $[\alpha]_D^{20}$ −37·2°, together with an *anhydride*, $(OH{\cdot}CH_2{\cdot}[CH(OH)]_8{\cdot}CO)_2O$, m. p. 250°. These were separated by taking advantage of the much greater solubility of the former compound. Both substances after hydrolysis yield the same *phenylhydrazide*, crystallising in rectangular lamellæ, m. p. 268°. The acid forms an ill-defined *amide*, $C_{10}H_{21}O_{10}N$, m. p. about 250°. The *sodium*, *barium*, *zinc*, *copper*, *lead*, and *cadmium* salts are sparingly soluble;

e *brucine*, *quinine*, *morphine*, and *strychnine* salts have been epared. W. O. W.

The Oxidation of Aldehydes in Alkaline Solution. GEORGE 7. HEIMROD and PHŒBUS A. LEVENE (*Biochem. Zeitsch.*, 1910, 29, 1—59).—The authors studied the oxidation of various substances i alkaline solution, using principally hydrogen peroxide as the idising agent, and, by means of a specially constructed apparatus hich is figured, estimated the hydrogen evolved, and also estimated ne carbon dioxide and formic acid formed. They confirmed the bservations of previous observers that formaldehyde yields on reatment with hydrogen peroxide, hydrogen gas, and assumed that he evolution of this gas is evidence of the formation of formldehyde as an intermediate product of oxidation when it is obtained rom other substances. Ethylene glycol, under the conditions of xidation chosen, evolved no hydrogen, whereas glycerol did, and the uthors give equations to represent what they consider to be the echanism of oxidation of this substance. They also investigated the xidation of acetaldehyde, and its possible intermediate oxidation roducts, glycollaldehyde, glyoxal, glycollic acid, and glyoxylic acid, stimating in each case the carbon dioxide and formic acids formed, and ive equations showing the various courses of oxidation possible. As a result of their experiment, they draw the conclusion that acetldehyde oxidises through the following stages: acetaldehyde (vinyl lcohol) → glycollaldehyde → glyoxal → formic acid → carbon lioxide. There is no evidence of the formation of formaldehyde as an ntermediate product. The reaction rates of the oxidation of acetldehyde under various conditions were also investigated. S. B. S.

Preparation of Aldehyde Diacetates. ALFRED WOHL and RUDOLF MAAG (*Ber.*, 1910, 43, 3291—3295. Compare Mannich and Häncu, Abstr., 1908, i, 245; Semmler, Abstr., 1909, i, 239, 312, 364, 594; Wohl and Berthold, Abstr., 1910, i, 620; Blanksma, Abstr., 1909, i, 779; Wegscheider and Späth, Abstr., 1910, i, 155).—It is pointed out that the formation of a monoacetate of the type R·CH:CH·OAc does not necessarily mean that the aldehyde exists in the tautomeric enolic form, as the monoacetates are formed at high temperatures only, whereas diacetates of the type $R·CH_2·CH(OAc)_2$ are formed at moderate temperatures, and it is highly probable that the monoacetates are formed by the decomposition of diacetates at the high temperature used:

$$R·CH_2·CH(OAc)_2 = R·CH:CH·OAc + AcOH.$$

It is shown that Wegscheider's yields can be materially improved if an excess of acetic anhydride is avoided; thus a 90% yield of acetaldehyde diacetate is formed when 1·25 mols. of aldehyde are used for 1 mol. of anhydride, and a 70% yield when equimolecular quantities are taken.

α-Keto-γ-acetoxyvaleric acid, $OAc·CHMe·CH_2·CO·CO_2H$, obtained by heating a mixture of molecular quantities of pyruvic acid, acetaldehyde, and acetic anhydride for five hours at 100° and distilling under reduced

pressure, is a colourless oil, b. p. 100—103°/12 mm. and does not decolorise bromine. Ethylidene diacetate is formed at the same time. A good yield of the latter can be obtained by heating lævulaldehyde with acetic anhydride and a few drops of concentrated sulphuric acid for an hour at 100°.

Acraldehyde diacetate, 64% yield, is best prepared at the ordinary temperature.

Phenylacetaldehyde diacetate, $CH_2Ph{\cdot}CH(OAc)_2$, has b. p. 147°/15 mm., and the monoacetate of the enolic form does not appear to be formed. A less volatile fraction, however, yields a small amount of glistening plates, $C_{20}H_{22}O_5$, probably $(CH_2Ph{\cdot}CH{\cdot}OAc)_2O$. J. J. S.

The History of Chemical Fermentation Hypotheses. Walther Löb (*Biochem. Zeitsch.*, 1910, **29**, 311—315).—A theoretical paper, in which the author, as a result of data obtained from his investigations on the action of the silent discharge on sugar solutions, etc., suggests that one molecule of sugar may first undergo scission into two molecules (glyceraldehyde or dihydroxyacetone), which themselves can undergo further scission into glycolladehyde and formaldehyde, and, finally, into formaldehyde only. Ethyl alcohol can be formed by reaction between glycolladehyde and formaldehyde, carbon dioxide being formed at the same time. Equations are given to explain the phenomena. S. B. S.

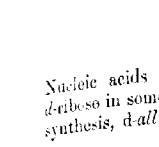
Mutarotation and Electrical Conductivity of Carbohydrates. I. Dextrose. Paul Rabe and Charles Roy (*Ber.*, 1910, **43**, 2964—2971).—*N*/10-Solutions of dextrose show no change in conductivity after twenty-four hours at 20°, during which the rotation falls from $[\alpha]_D^{20}$ +97·5° to +56°. No change was observed even with the most delicate instruments after five months' further keeping. E. F. A.

β-Dextrose. Robert Behrend (*Annalen*, 1910, **377**, 220—223).—The separation of β-dextrose by cooling a hot solution of α-dextrose in pyridine (Abstr., 1907, i, 481) can only be explained if the β-dextrose crystallises with pyridine. If the β-dextrose separates as such, it is possible by selecting two suitable solvents at the same temperature and pressure to create a system in which perpetual motion must occur. It is shown that the β-dextrose does separate in crystals, which rapidly weather and lose pyridine in amount corresponding approximately with 1 molecule of pyridine of crystallisation.

The author arrives at the same result as Dimroth (compare this vol., ii, 31), namely, that the same substance must always separate from solutions, at the same temperature and pressure, of two mutually interconvertible isomerides in any solvent, provided that by-products are not formed. C. S.

Hexoses from *d*-Ribose. Phœbus A. Levene and Walter A. Jacobs (*Ber.*, 1910, **43**, 3141—3147).—The four unknown aldohexoses are theoretically to be derived from the isomeric riboses, but the lack of these pentoses, has hitherto prevented the synthesis of the hexoses.

Nucleic acids now afford a relatively simple means of obtaining *d*-ribose in some quantity, and by the application of the cyanohydrin synthesis, d-*allose* and d-*altrose* have been obtained. They have the annexed configuration.



d-Allose. *d*-Altrose.

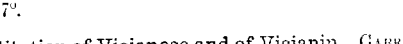
Both are syrups insoluble in alcohol, and have not been obtained free from impurities. They yield the same phenylosazone, and *d*-altronic acid yields talomucic acid on oxidation.

Calcium d-*altronate* is obtained by the addition of hydrogen cyanide to *d*-ribose and hydrolysis of the nitrile formed with barium hydroxide. The solution is rendered slightly acid, and treated in turn with lead carbonate, hydrogen sulphide, and calcium carbonate. It crystallises in thick crusts of cauliflower-like aggregates of needles. The free *acid* is a colourless syrup; the specific rotatory power increases in solution, $[\alpha]_D^{20}$ +35·14°.

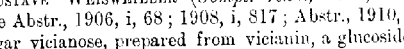
On reduction, *d*-altrose is obtained as a syrup. The *phenylbenzylhydrazone* crystallises in well formed, yellow, lustrous plates, which sinter at 145°, m. p. 148—150° (corr.). d-*Altrosephenylosazone*, crystallises in long, thin, matted needles or stellate aggregates of platelets, which sinter at 175°, m. p. 183—185° (corr.). It is lævorotatory in pyridine solution.

The mother liquors from the calcium altronate contain calcium allonate. d-*Allonolactone*, $C_6H_{10}O_6$, forms long, colourless prisms, which sinter at 97° and are completely melted to a clear liquid at 120°, and have $[\alpha]_D^{20}$ −6·79° (± 0·2°). d-*Allose*-p-*bromophenylhydrazone* crystallises in lustrous plates, which sinter at 143°, m. p. 145—147° (corr.), $[\alpha]_D^{20}$ −6·7°. E. F. A.

Constitution of Vicianose and of Vicianin. Gabriel Bertrand and Gustave Weisweiller (*Compt. rend.*, 1910, 151, 884—886. Compare Abstr., 1906, i, 68; 1908, i, 817; Abstr., 1910, i, 156).—The new sugar vicianose, prepared from vicianin, a glucoside occurring in the vetch, has been oxidised by bromine water in presence of calcium carbonate. A calcium vicianobionate was thus obtained, which on hydrolysis gave calcium gluconate and *l*-arabinose. Vicianose, therefore, appears to have the constitution:



whilst the glucoside is represented as:



The other properties of the substances described previously are in agreement with these representations. W. O. W.

The Degradation of the Sugar Group. Adolf Jolles (*Biochem. Zeitsch.*, 1910, **29**, 152—201).—It is shown that the majority of the sugars undergo chemical change at 37° when treated with *N*/100-

alkali hydroxide, the optical rotation of the solution decreasing and the acidity increasing. The latter change continues after the former change has ceased. In certain cases, as, for example, that of sucrose, the change is small. The rate of acid formation is increased by the addition of hydrogen peroxide and silver oxide, although the addition of oxidising reagents does not affect the rate of change in optical activity. Ferments exert but slight influence. If sugars be kept in alkaline medium, the estimation by polariscope becomes, owing to the above-mentioned changes, untrustworthy, although they do not affect the reducing powers. Formic acid and, in case of certain sugars, acetaldehyde were detected as reaction products. Polyhydroxy-acids were not found. The author gives a large number of data showing the rate of the changes in various sugars. S. B. S.

Mutarotation of Maltose. GERHARD SCHLIEPHACKE (*Annalen*, 1910, **377**, 164—188).—The theory that the mutarotation of a sugar in solution is due to the equilibrium of the two stereoisomeric lactone forms of the sugar with one another, and probably also with the aldehydic form, is supported by the relations which have been shown to exist between dextroses of different rotatory powers and their penta-acetates (Behrend and Roth, Abstr., 1904, i, 716), and between galactoses of different rotatory powers and their penta-acetates (Heikel, Abstr., 1905, i, 173). The author has now examined a biose, maltose, with regard to its mutarotation and its acetates. Dissolved in pyridine, the sugar has $[\alpha]_D^{20}$ + 97·7° forty minutes after solution, and 122·2° after fourteen days; after being warmed to 50° for ten minutes, the solution attains a constant rotatory power, $[\alpha]_D^{20}$ + 123·5°. After being boiled for three minutes and then cooled, the solution attains its maximum rotation, having $[\alpha]_D^{24}$ + 128·8°, which falls to 124·0° after one hundred and thirty-two hours.

Ordinary maltose belongs probably to the β-series, since it yields, when acetylated under suitable conditions, chiefly the only known crystalline acetate, Herzfeld's maltose octa-acetate, m. p. 155—156°, which belongs to the β-series, having been converted into β-methyl-glucoside by Königs and Knorr. When solid maltose in the presence of pyridine at 0° is treated with acetic anhydride, it yields a crude acetate, from which 73·9% of crystallised β-octa-acetate has been obtained together with a syrup which has the composition of an octa-acetate and $[\alpha]_D$ + 101·3° in benzene. When a solution of maltose in pyridine, of constant rotation, is acetylated at 0°, 36·1% of the crystallised β-octa-acetate and a syrup having $[\alpha]_D$ + 107·1° in benzene are obtained. Finally, when the pyridine solution of maximum rotation obtained by boiling is acetylated at 0°, only 18·8% of the crystallised β-octa-acetate is obtained, together with a syrup having $[\alpha]_D$ + 110·6°. These results indicate that the solution of maltose in pyridine contains ordinary β-maltose (which yields the β-octa-acetate) in equilibrium with another or, more probably, two other forms of maltose (which yield the syrup). The rotation of the unknown α-maltose octa-acetate, calculated by Hudson's theory (Abstr., 1909, i, 135), corresponds with $[\alpha]_D$ + 131·88° in benzene and + 117·51° in chloroform; the values are given with reserve, since it is as yet

uncertain whether Hudson's theory is applicable to the acetates of the sugars.

When maltose is acetylated in pyridine there is produced, together with the octa-acetates, about 6% of a *hexa-acetate*, which is an amorphous powder having $[\alpha]_D + 133{\cdot}96°$ in benzene and $139{\cdot}96°$ in chloroform; it separates together with the β-octa-acetate from alcoholic solutions, and is separated therefrom mechanically.

By treating β-maltose octa-acetate with liquid hydrogen chloride, Fischer and Armstrong obtained a hepta-acetylchloromaltose having m. p. 66—68° and $[\alpha]_D^{20} + 176{\cdot}0 \rightarrow 177{\cdot}1°$ in benzene. By treating maltose with acetic anhydride and hydrogen chloride, Foerg obtained a hepta-acetylchloromaltose having m. p. 118—120° and $[\alpha]_D - 159°$ in chloroform. The author hoped to get α-maltose octa-acetate from the latter, but by treatment with glacial acetic acid and anhydrous sodium acetate on the water-bath, it yielded the β-isomeride. The author confirms Foerg's m. p. for the substance, but finds that it has $[\alpha]_D + 158{\cdot}68°$ in chloroform and $175{\cdot}66°$ in benzene, the latter value being almost identical with the corresponding value of Fischer and Armstrong's compound. The relation between these two substances, having the same rotatory power but different m. p.'s, has not yet been ascertained; both give the same β-hepta-acetylmethylmaltoside by treatment with methyl alcohol and silver carbonate. C. S.

Carbohydrates Occurring in Seeds. ERNST SCHULZE and URS PFENNINGER (*Zeitsch. physiol. Chem.*, 1910, 69, 366—382).—A large number of plant seeds contain soluble carbohydrates that give mucic acid on oxidation with nitric acid, and therefore yield galactose on hydrolysis. Raffinose is known to occur in cotton seed, in the embryos of wheat, and of certain leguminous plants; the authors now describe another carbohydrate, *lupeose*, which has not yet been crystallised, but is, they believe, a single substance and not a mixture.

Lupeose has been extracted from seeds of *Lupinus luteus* and *Lupinus angustifolius* by extraction either with hot dilute alcohol or with water; it is then obtained from this solution by precipitation with alcohol. It forms a white powder, readily soluble in water, and does not reduce Fehling's solution until it has been heated with acids. It is dextrorotatory; the different preparations in 4 or 5% solution have given $[\alpha]_D = +138°$ to $+144°$, the differences no doubt arising from the presence of impurities. Oxidation with nitric acid gives rise to 38—40% of mucic acid; presumably, therefore, galactose constitutes half of the products of hydrolysis. Lævulose is also formed on hydrolysis, and there appears to be a third sugar. For this and other reasons lupeose is considered to be more complex than a disaccharide. In several ways lupeose resembles stachyose, but the differences are sufficient to justify the conclusion that the two are distinct. E. J. R.

Mercerised Cellulose. OSWALD MILLER (*Ber.*, 1910, 43, 3430—3435. Compare Vieweg, Abstr., 1907, i, 893; Schwalbe, *ibid.*, 1909, i, 136, 366).—If cellulose is dried for six hours at 95° both before and after

treatment with concentrated sodium hydroxide solution at 10° there is practically no alteration in weight. The loss in weight of the mercerised product when dried at 95° is the same as when the drying takes place at 22—23° over calcium chloride. Analyses also show that the mercerised and not mercerised compounds have the same percentage composition. That the compounds, however, are not identical has been proved by Wichelhaus and Vieweg (Abstr., 1907, i, 186) by an examination of the products of nitration, and is confirmed by the fact that the amount of water adsorbed by mercerised cellulose is much greater than by ordinary cellulose. The degree of mercerisation can be determined especially by dyeing with rosaniline base; with substantive dyes of the type of geranin-G and chrysophenin an increase in the depth of colour is observed only after the cellulose has been treated with 9% sodium hydroxide solution, and then the colour increases with the concentration of the alkali up to, and probably beyond, 25%. J. J. S.

The Reaction between Humin and Potassium Hypobromite. ARTUR KONSCHEGG (*Zeitsch. physiol. Chem.*, 1910, **69**, 390—394).—The humin was obtained from dextrose by heating 250 grams for twelve hours with 1 litre of 24% hydrochloric acid; the brown flocks produced were then treated with aqueous potassium hydroxide to dissolve out humic acid. The residual humin forms a viscid, mucilaginous mass, that can only with difficulty be separated by filtration from the alkaline solution of humic acid. When dried at 100° it forms a glassy, brittle mass, that breaks down to a powder much darker than humic acid. It is insoluble in water, acids, alkalis, alcohol, or ether.

When, however, humin is suspended in potassium hydroxide and a little bromine added, it passes into solution. After a time, white crystals of tetrabromomethane separate. Humic acid behaves in the same way.

The author finds that humic acid dissolves in water to form a colloidal solution. If the precipitate obtained by adding hydrochloric acid to the alkaline solution of humic acid is washed with water, the filtrate soon begins to be coloured. The dark liquid on evaporation leaves a black, caseous residue soluble both in water and alcohol.

E. J. R.

Chloro-salts of Osmium. ALEXANDER GUTBIER [with K. MAISCH] (*Ber.*, 1910, **43**, 3234—3239).—The substituted ammonium osmichlorides described were prepared by the interaction of the respective substituted ammonium chlorides with sodium osmichloride (Abstr., 1910, ii, 45), than which they are much less soluble; they are all anhydrous and stable in the air. In aqueous solution they undergo decomposition, but in hydrochloric acid solution they are stable. In some cases they are readily soluble in alcohol.

Methylammonium osmichloride, $(NH_3Me)_2OsCl_6$, reddish-brown, anisotropic crystals. *Dimethylammonium osmichloride*, $(NH_2Me_2)_2OsCl_6$, yellowish-red, rhombic prisms, which are pleochroic. *Trimethyl-*

ammonium osmichloride, $(NHMe_3)_2OsCl_6$, light yellowish-red, regular crystals. *Ethylammonium osmichloride*, $(NH_3Et)_2OsCl_6$, scarlet-red, pleochroic leaflets. *Diethylammonium osmichloride*, $(NH_2Et_2)_2OsCl_6$, yellowish-red, monoclinic crystals. *Triethylammonium osmichloride*, $(NHEt_3)_2OsCl_6$, reddish-yellow, monoclinic needles. *n-Propylammonium osmichloride*, $(NH_3Pr^{\alpha})_2OsCl_6$, dark brownish-red, monoclinic crystals. *isoPropylammonium osmichloride*, $(NH_3Pr^{\beta})_2OsCl_6$, brownish-red, pleochroic crystals. *Dipropylammonium osmichloride*, $(NH_2Pr_2)_2OsCl_6$, reddish-yellow, monoclinic prisms. *n-Butylammonium osmichloride*, $(NH_3{\cdot}C_4H_9)_2OsCl_6$, brownish-red, monoclinic crystals. *isoButylammonium osmichloride*, $(NH_3{\cdot}C_4H_9)_2OsCl_6$, dark brownish-red, monoclinic or rhombic crystals. *Ethylenediammonium osmichloride*, $C_2H_{10}N_2OsCl_6$, dark brown, monoclinic crystals. *Propylenediammonium osmichloride*, $C_3H_{12}N_2OsCl_6$, dark brownish-red, monoclinic crystals.

T. S. P.

Nitrilo-trimethylnitroaminomethylene. ANTOINE P. N. FRANCHIMONT (*Rec. trav. chim.*, 1910, [ii], **14**, 355—367.* Compare Abstr., 1910, i, 616, 617; Eschweiler, Abstr., 1894, i, 267).—An investigation (1) of the conditions under which hexamethylenetetramine and methylnitroamine react to form nitrilo-trimethylnitroaminomethane, $N(CH_2{\cdot}NMe{\cdot}NO_2)_3$, and (2) of the constitution of the latter. This substance is formed in small quantity when hexamethylenetetramine is mixed in aqueous solution with methylnitroamine and boiled for some days, but a better yield is obtained when water is replaced by a solution of formaldehyde, and a quantitative yield when the decomposition products of hexamethylenetetra-amine, namely, formaldehyde and ammonia, are mixed with methylnitroamine and slightly warmed.

Nitrilo-trimethylnitroaminomethane, m. p. 116°, crystallises in colourless, transparent prisms, and gives the nitroamine reaction with zinc and α-naphthylamine. When boiled with alkalis, it decomposes in accordance with the equation $N(CH_2{\cdot}NMe{\cdot}NO_2)_3 + 3H_2O = NH_3 + 3H{\cdot}CHO + 3NHMe{\cdot}NO_2$, whilst with acids the reaction takes place as follows: $N(CH_2{\cdot}NMe{\cdot}NO_2)_3 + 3H_2O = NH_3 + 3H{\cdot}CHO + 3N_2O + 3CH_2OH$. In the former case some of the ammonia combines with the formaldehyde, and the reaction cannot be followed quantitatively, but in the second case ammonia, formaldehyde, and nitrous oxide can be estimated, and the results of these estimations serve to establish the constitution of the substance. When dissolved in chloroform and treated with hydrogen chloride, a crystalline *hydrochloride*,

$$NO_2{\cdot}NMe{\cdot}CH_2{\cdot}NH_2,HCl,$$

is formed, which, on evaporation of its aqueous solution, evolves hydrogen chloride and forms a mixture of ammonium chloride, and a soluble substance giving the nitroamine reaction. T. A. H.

Synthesis of γ-Amino-α-hydroxybutyric Acid and its Trimethyl Derivative. EMIL FISCHER and ALBERT GÖDDERTZ (*Ber.*, 1910, **43**, 3272—3280. Compare Fischer and Zemplén, Abstr., 1910, i, 100).—*γ-Phthalimino-α-hydroxybutyric acid*,

$$C_6H_4(CO)_2{:}N{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H,$$

can be obtained by boiling the corresponding α-bromo-acid (Gabriel

* and *Proc. K. Akad. Wetensch. Amsterdam*, 1910, **13**, 527—530.

and Colman, Abstr., 1908, i, 274) with water and calcium or barium carbonate for about fifteen minutes. The *calcium* salt,

$$Ca(C_{12}H_{10}O_5N_2)_2,6H_2O,$$

crystallises from water at 0° in colourless crusts of minute prisms. The *barium* salt also crystallises with $6H_2O$, and when treated with a slight excess of dilute sulphuric acid yields the free acid, which crystallises from hot water in long, colourless needles, containing $1H_2O$, and melting at about 100°; when anhydrous it has m. p. 144—145° (corr.). It has a feebly acidic, but strongly astringent, taste. When hydrolysed with concentrated hydrochloric acid in a platinum flask, it yields *γ-amino-α-hydroxybutyric acid hydrochloride* and phthalic acid. The *hydrochloride*, $C_4H_9O_3N,HCl$, crystallises from a mixture of alcohol and ethyl acetate in colourless needles. The *platinichloride* crystallises from warm alcohol in orange-coloured plates; the *acid*, $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H$, crystallises from dilute alcohol, and has m. p. 191—192° (corr.). It has no characteristic taste, is not precipitated by phosphotungstic acid, and when heated at 210° for five minutes yields *3-hydroxypyrrolidone*, $OH{\cdot}CH<\begin{matrix}CH_2{\cdot}CH_2\\ CO-NH\end{matrix}$, which crystallises from ethyl acetate at 0° in thin plates, m. p. 85° (corr.). It has a sweet taste, yields a crystalline mercury derivative, and is partly hydrolysed to the amino-acid when boiled with 25% hydrochloric acid. The pyrrolidone is also formed when an alcoholic solution of the amino-acid is saturated with hydrogen chloride.

α-Hydroxy-γ-trimethylaminobutyric acid is formed when the amino-acid is exhaustively methylated. The *sulphate* is readily soluble in water; the *aurichloride*, $C_7H_{15}O_3N,HAuCl_4$, crystallises in yellow needles, m. p. 175—176° (corr.) after sintering at 162°. The *hydrochloride* and *platinichloride* are syrups which crystallise slowly. The latter crystallises in long, slender needles, m. p. 216° (decomp.). The methyl derivative is probably identical with *dl*-carnitine. J. J. S.

Preparation of Creatinine from Urine. Otto Folin and Frederick C. Blanck. **Preparation of Creatinine from Creatine.** Otto Folin and W. Denis (*J. Biol. Chem.*, 1910, 8, 395—397, 399—400).—Details are given of the picric acid procedure in the separation of creatinine from urine. Creatine may be converted into creatinine without the use of any solvent or acid. The water of crystallisation of creatine is sufficient. If creatine is placed in a closed bottle and heat applied until a pressure of 4·5 kilos. per square centimetre is reached, and this is kept up for three hours, the contents contain crystalline creatinine. W. D. H.

Creatinine. Ernst Schmidt (*Arch. Pharm.*, 1910, **248**, 568—578).—Mainly an introduction to the two following papers, the object of which is the confirmation of Pommerehne and Toppelius' statement that the creatinines from flesh, from urine, or synthetically produced, are all identical (Abstr., 1897, i, 128), not different as claimed by Johnson (Abstr., 1889, 165).

Neubauer's statement (*Annalen*, 1861, **119**, 49) that creatinine when alkylated behaves as a tertiary base has been denied by

Korndörfer (Abstr., 1904, i, 768), whose results are now confirmed by the fact that creatinine by methylation yields first methylcreatinine, $NMe<\begin{matrix}CH_2\cdot CO\\ C(:NH)\end{matrix}>NMe$, and then dimethylcreatinine,

$$NMe<\begin{matrix}CH_2-CO\\ C(:NMe)\end{matrix}>NMe;$$

the latter then behaves as a tertiary base. C. S.

Methyl-, Dimethyl-, and Trimethyl-creatinines. Gerhard Kunze (*Arch. Pharm.*, 1910, **248**, 578—593).—The methylation of creatinines produced synthetically or from flesh yields methylcreatinine hydriodides, which are identical, and from which identical hydrochlorides, aurichlorides, and platinichlorides are obtained. All these compounds are identical with the corresponding substances obtained by Korndörfer (Abstr., 1905, i, 152) from creatinine prepared from urine.

The base liberated from the methylcreatinine hydriodide by potassium carbonate, lead oxide, or silver oxide is hydrolysed by boiling baryta, yielding carbon dioxide, ammonia, methylamine, and sarcosine, and is oxidised by alkaline 5% potassium permanganate at 50—60° to oxalic acid and Schenck's *s*-dimethylguanidine (Abstr., 1910, i, 99); consequently, the methylcreatinine has the constitution $NH:C<\begin{matrix}NMe\cdot CH_2\\ |\\ NMe\cdot CO\end{matrix}$. By further methylation at 50—70°, it yields dimethylcreatinine hydriodide, m. p. 179—180°; *aurichloride*, m. p. 128—129°; platinichloride, m. p. 177—179° (not 169—170°), the base in which has the constitution $NMe:C<\begin{matrix}NMe\cdot CH_2\\ |\\ NMe\cdot CO\end{matrix}$, since it is oxidised by alkaline potassium permanganate to oxalic acid and Schenck's trimethylguanidine (*loc. cit.*). C. S.

Ethylcreatinine. Carl Henzerling (*Arch. Pharm.*, 1910, **248**, 591—608).—The work is very similar to that of Kunze (preceding abstract), and proves that creatinines obtained from different sources are identical. When alkylated by ethyl iodide, creatinine behaves like a secondary base, yielding *ethylcreatinine hydriodide*,

$$C_6H_{11}ON_3HI,$$

m. p. 217—219° (from which are formed an *aurichloride* and a *platinichloride*, m. p. 197—211°, monoclinic plates, $a:b:c=0\cdot8685:1:0\cdot7385$, $\beta=86°24\cdot5'$), and also creatinine hydriodide, m. p. 195°, as a by-product. The ethylcreatinine hydriodide cannot be an ethiodide, as stated by Neubauer, because the chloride prepared from it is decomposed by potassium carbonate, yielding ethylcreatinine, which has not been obtained crystalline. It is oxidised by alkaline potassium permanganate to oxalic acid and methylethylguanidine (*platinichloride*, m. p. 179—181°), and is hydrolysed by boiling barium hydroxide, yielding carbon dioxide, ammonia, ethylamine, and sarcosine. By treatment with ethyl iodide at 100°, ethylcreatinine yields chiefly ethylcreatinine hydriodide, small quantities of ethylamine and diethylcreatinine (*platinichloride*, m. p. 201—202°) also being formed.

When ethylcreatinine is treated with methyl iodide, the chief product is again ethylcreatinine hydriodide, methylamine and a small amount of methylethylcreatinine (*platinichloride*, m. p. 181—182°) also being formed. C. S.

Propiolic Compounds. Cyanoacetylene, C_3HN. Charles Moureu and J. Charles Bongrand (*Compt. rend.*, 1910, 151, 946—948. Compare Abstr., 1910, i, 159).—*Propiolamide*,

$$CH{:}C{\cdot}CO{\cdot}NH_2,$$

has been obtained by the action of aqueous ammonia at 0° on methyl propiolate. It occurs in lamellæ, m. p. 61—62°; the aqueous solution forms a white precipitate with silver nitrate, and a yellow one with ammoniacal cuprous chloride. When distilled with phosphoric oxide in an atmosphere of carbon dioxide under diminished pressure, cyanoacetylene, $CH{:}C{\cdot}CN$, is obtained as a colourless, mobile liquid, b. p. 42·5°/760 mm., D_4^{17} 0·8159, solidifying to crystals, m. p. 5°. The compound is inflammable, and becomes brown on keeping, even in absence of light and air. The vapour is intensely irritating. With silver nitrate, it forms a white explosive substance, whilst the compound obtained by the action of ammoniacal cuprous chloride is green and deflagrates on heating. The molecular refractions for the *D*-sodium line and for the *α*-, *β*-, and *γ*-hydrogen lines have been determined at 17°: M_D 14·7207; $M_\gamma - M_\alpha$ 0·563. Owing to the presence of the acetylenic linking, the refraction and dispersion are higher than the calculated values.

The action of potassium ferricyanide on cyanoacetylene gives rise to a product, which, when sublimed in an atmosphere of carbon dioxide, yields colourless needles, m. p. 64°. This substance has an irritating odour, and the author believes it to be a new carbon subnitride, C_6N_2. W. O. W.

Catalytic Action. IV. Comparison of the Action of Various Catalytic Agents. II. Acetylation of Carbamide. Jacob Böeseken [with Mlle. J. Langezaal] (*Rec. trav. chim.*, 1910, 29, 330—339. Compare Abstr., 1910, i, 152).—Geuther first effected the acetylation of carbamide, and showed the formation of only a small amount of cyanuric acid, thus differing from the behaviour of the symmetrical di-substituted products of carbamide. The authors show that the difference in behaviour of carbamide and its derivatives is quantitative rather than qualitative.

Various catalytic agents were used in the acetylation, and the results obtained, showing their relative influence and the amounts of acetylcarbamide and cyanuric acid formed, are tabulated in the original.

Various salts of cyanuric acid were made to try and effect its estimation, and the *strontium* salt is described. It was found more convenient to estimate the acid by titration with dilute potassium hydroxide, the acetylcarbamide not being affected.

It was found that on prolonged heating with the catalytic agents, acetylcarbamide is partly decomposed, the percentage of cyanuric acid present increasing. N. C.

Nitrogen and Sulphur Derivatives of Carbon Disulphide. XVII. Tetra-alkylthiocarbamides and Tetra-alkyl*iso*thiocarbamides. MARCEL DELÉPINE (*Bull. Soc. chim.*, 1910, [iv], 7, 988—993).—Compounds of these two types have been prepared previously, but have not been described in detail, and in this paper an account is given of their preparation, properties, and chief derivatives.

The tetra-alkylthiocarbamides are best obtained by Billeter's method, which consists in treating the appropriate secondary amine in benzene or toluene with thiocarbonyl chloride. The tetramethyl compound may be obtained from von Braun and Stechele's tetramethylthiouram sulphide (Abstr., 1903, i, 618) by the action at 100° of dimethylamine dissolved in benzene, thus: $S(CS\cdot NMe_2)_2 + 2NMe_2 = NMe_2\cdot CS\cdot NMe_2 + NMe_2\cdot CS\cdot S\cdot NH_2Me_2$, dimethylamine dimethyldithiocarbamate being also formed. The same two substances result from the action of dimethylamine on dimethylthiouram disulphide: a method analogous with that used by Fromm (Abstr., 1909, i, 506).

The tetra-alkyl*iso*thiocarbamides are obtained by the action of the necessary alkyl iodide on the trialkylthiocarbamides.

The two series of compounds differ considerably in properties. The tetra-alkylthiocarbamides are usually of higher specific gravity and boiling point than their isomerides, and are not basic, whilst their isomerides are markedly basic up to the tetrapropyl compound, which on titration in presence of the usual indicators appears to be saturated before one equivalent of acid has been added. The members of both groups form additive compounds with one mol. of methyl iodide.

Tetramethylthiocarbamide, $S:C(NMe_2)_2$, m. p. 78°, b. p. 245°, is readily soluble in warm, but less so in cold, water (compare Billeter, Abstr., 1910, i, 544). The *methiodide*, $SMeI:C(NMe_2)_2$ or $SMe\cdot CI(NMe_2)_2,H_2O$, crystallises from alcohol in colourless prisms. On treatment with silver nitrate followed by ammonia, it yields silver methylmercaptide. *Tetraethylthiocarbamide*, b. p. 130°/12 mm., 264—266°/760 mm., D_4^0 0·9804, D_4^{18} 0·9662, is an oily liquid of pleasant odour. *Tetrapropylthiocarbamide*, b. p. 165°/12 mm., or about 305°/760 mm., D_4^0 0·9430, D_4^{20} 0·9300, is a viscid, almost inodorous liquid.

*Tetramethyliso**thiocarbamide*, $NMeI:C(SMe)\cdot NMe_2$, b. p. 176°, D_4^0 1·0194, D_4^{16} 1·0061, is a colourless liquid of strong odour. The *picrate*, m. p. 99·5°, crystallises in yellow needles. Tetraethyl*iso*thiocarbamide has b. p. 216°, D_4^0 0·9426, D_4^{21} 0·9252 (Grodzky, Abstr., 1882, 823). *Tetrapropyliso**thiocarbamide*, b. p. 154°/15 mm., 270°/760 mm. (decomp.), D_4^0 0·9179, D_4^{21} 0·9014, is a colourless, oily liquid of slight odour. It was prepared by the general method from *tripropylthiocarbamide*, m. p. 33°, which crystallises in colourless needles, and was obtained by the union of dipropylamine with propylthiocarbimide. T. A. H.

Formation of Fulminic Acid from Alcohol. HEINRICH WIELAND (*Ber.*, 1910, **43**, 3362—3364).—Polemical against Wöhler (Abstr., 1910, i, 231). The following details for the preparation of mercury fulminate from oximinoacetic acid are given. 1·5 Grams of oximinoacetic acid are added to a solution of 1 gram of mercuric

nitrate in 3 c.c. of nitric acid (D = 1·34) and 2 c.c. of water. If the reaction is allowed to go on of its own accord, without cooling, 0·1—0·2 gram of mercury fulminate is obtained, whereas when the reaction is moderated no fulminate is formed. Silver fulminate is obtained in a similar manner. T. S. P.

Chloralurethane. II. Otto Diels and Armenak Gukassianz (*Ber.*, 1910, **43**, 3314—3320. Compare Abstr., 1909, **i**, 885).—The constitution, $CCl_2{:}C(CN)\cdot NH\cdot CO_2Et$, of the nitrile obtained by boiling the acetyl derivative of chloralurethane with aqueous potassium cyanide has been proved by the behaviour of the substance towards ozone and towards nitric acid. The former converts it into carbonyl chloride and a substance (probably $CN\cdot CO\cdot NH\cdot CO_2Et$) which yields oxalic acid by hydrolysis. Warm concentrated nitric acid converts the nitrile into dichlorodinitromethane and oxalic acid.

The action of ethylamine, aniline, piperidine, and sodium ethoxide on the nitrile also supports the constitution. An ethereal solution of the nitrile and ethylamine at 0° yield the *substance*,

$$C(NHEt)_2{:}C(CN)\cdot NH\cdot CO_2Et,$$

m. p. 104° (corr.), flat plates. The nitrile and aniline, after being heated on the water-bath for one and a-half hours, yield the *substance*, $C(NHPh)_2{:}C(CN)\cdot NH\cdot CO_2Et$, m. p. 166—167° (corr.). The nitrile and piperidine in ether yield a corresponding substance which, however, cannot be isolated, but is converted by concentrated hydrochloric acid into the *piperidide*, $C_5NH_{10}\cdot CO\cdot C(CN)\cdot NH\cdot CO_2Et$, m. p. 131·5—132·5° (corr.). The nitrile is converted by alcoholic sodium methoxide or sodium ethoxide into the *ortho*-esters,

$$C(OMe)_3\cdot CH(CN)\cdot NH\cdot CO_2Et,$$

m. p. 86—87° (corr.), and $C(OEt)_3\cdot CH(CN)\cdot NH\cdot CO_2Et$, m. p. 56°; when the former is boiled with glacial acetic acid it is converted into *methyl cyanocarbethoxyglycine*, $CO_2Me\cdot CH(CN)\cdot NH\cdot CO_2Et$, m. p. 130·5° (corr), which is easily soluble in alkalis. C. S.

Synthetical Experiments in the Cincholeupone Series. Alfred Wohl and Rudolf Maag (*Ber.*, 1910, **43**, 3280—3291).—Attempts have been made to synthesise cincholeupone derivatives, but, so far, without success. A dimethylpiperidine has been prepared by the following method:

By the addition of ethyl sodiocyanoacetate to the condensation product of aldehyde and acetone, ethyl α-cyano-γ-acetyl-β-methyl butyrate, $CO_2Et\cdot CH(CN)\cdot CHMe\cdot CH_2Ac$, is formed, and when this is hydrolysed and reduced, 2 : 4-dimethylpiperidine is formed.

A fairly good yield of ethylideneacetone (Claisen, Abstr., 1893, i, 8) is obtained by saturating a well cooled mixture of paraldehyde and acetone with dry hydrogen chloride and leaving for two days at 0°. The product obtained by distillation contains appreciable amounts of chlorine, but can be obtained pure by distilling twice over diethylaniline. An impure product, b. p. 120—130°, was used for the condensation with ethyl sodiocyanoacetate. The condensation product, $C_{10}H_{15}O_3N$, has b. p. 155—168°/14 mm., and when hydrolysed with 5*N*-sodium hydroxide solution and distilled, gives a 50% yield

of δ-*keto*-β-*methylvaleronitrile*, $COMe\cdot CH_2\cdot CHMe\cdot CH_2\cdot CN$, b. p. 105° 11 mm.

The *amide*, $COMe\cdot CH_2\cdot CHMe\cdot CH(CN)\cdot CO\cdot NH_2$, obtained by shaking the cyano-ester with ammonium hydroxide solution, crystallises from alcohol or water, and has m. p. 134°.

The nitrile forms a definite compound with hydrogen chloride, $2C_7H_{11}ON,HCl$, in the form of colourless crystals. The nitrile is not affected by zinc dust and acetic acid, zinc dust and ammonia, sodium amalgam and dilute alcohol, but is reduced by sodium and boiling amyl alcohol, yielding small amounts of 2 : 4-*dimethylpiperidine*, $C_7H_{15}N$, which, after careful fractionation, has b. p. 136—138°. The *oxalate*, $C_7H_{15}O_4N,\frac{1}{2}H_2O$, crystallises in nacreous needles, m. p. 134°, after sintering at 130°. A small amount of ε-*hydroxy*-γ-*methylhexylamine*, $NH_2\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot CHMe\cdot OH$, is also formed during the reduction; it has b. p. 119—120°/12 mm., and yields an *oxalate*, $C_{10}H_{19}O_5N$, with m. p. 142—145°. The amine reacts at 100—115° with a solution of hydrobromic acid saturated at below 0°, yielding an unsaturated *base* isomeric with dimethylpiperidine. It has b. p. 145—150°, and yields an *oxalate*, m. p. 150°. One of the formulæ $NH_2\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH{:}CHMe$ or

$$NH_2\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot CH{:}CH_2$$

is suggested.

Acetone does not condense with acraldehyde in the presence of hydrogen chloride; the only product appears to be mesityl oxide. The condensation takes place in the presence of a small amount of potassium cyanide, but the additive product formed polymerises with the greatest readiness. Definite products could not be isolated by condensing acraldehyde with ethyl acetoacetate in the presence of piperidine or potassium cyanide at −10°.

Ethoxypropaldehydediethylacetal and ethyl acetoacetate condense in the presence of glacial acetic acid and a little concentrated sulphuric acid or zinc chloride, yielding a product,

$$OEt\cdot CH_2\cdot CH_2\cdot CH{:}CAc\cdot CO_2Et,$$

with b. p. 142—144°/11 mm. This product is unsaturated, and readily decolorises solutions of bromine and permanganate.

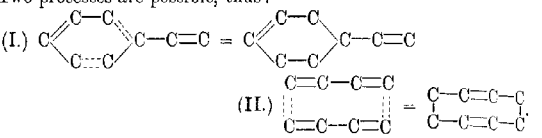
Claisen's β-hydroxypentan-δ-one is formed when one-eighth of the amount of potassium cyanide recommended by Claisen is used for the condensation of aldehyde and acetone. Phosphorus tribromide reacts with an ethereal solution of the hydroxy-compound, yielding *β-bromopentan-δ-one*, $CH_3\cdot CHBr\cdot CH_2\cdot COMe$, with b. p. 50—55°/15 mm. The bromo-derivative is extremely unstable, and when kept for several days is transformed into a dark brown syrup. It condenses with ethyl sodiocyanoacetate, yielding ethyl α-cyano-γ-acetyl-β-methylbutyrate. J. J. S.

Catalytic Reactions at High Temperatures and Pressures. XX. Dehydration of Cyclic Alcohols. Wladimir N. Ipatieff (*Ber.*, 1910, **43**, 3383—3387).—It has been shown previously (Abstr., 1903, i, 593; 1904, ii, 644; 1907, i, 6) that alcohols may be dehydrated in contact with alumina that has been only gently heated, ethers being formed at first, and then olefines.

Cyclic polyhydric alcohols may be dehydrated by heating with alumina in an atmosphere of hydrogen under a pressure of 30—40 atmospheres. Quinitol yields *cyclo*hexadiene with a little *cyclo*hexene at 350°, a good yield of the latter compound being obtained from *cyclo*hexanol. 1-Methyl*cyclo*hexan-2-ol yields methyl*cyclo*hexene in a mixture of several isomerides. Decahydro-β-naphthol yields octahydronaphthalene. C. H. D.

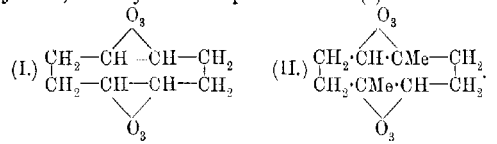
Polymerisation of Diethylene Hydrocarbons of the Type C:C·C:C. S. V. LEBEDEFF (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 949—961).—The polymerisation of hydrocarbons with a system of double bonds is so typical that it can be regarded as a general characteristic of these compounds; the temperature, however, greatly influences the velocity of the reaction and the character of the products; the latter, on the other hand, does not depend on the period of heating.

Two processes are possible, thus:

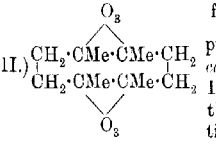


The lower the temperature the more is the 8-membered ring obtained. Light also favours process (II).

Divinyl heated in a sealed tube at 150° for six or seven days forms: (1) *Ethenyl*cyclo*hexene*, $CH\leqslant\begin{matrix}CH_2—CH_2\\CH—CH_2\end{matrix}>CH\cdot CH{:}CH_2$, b. p. 66° 100 mm., 131°/760 mm., D_0^{20} 0·8321. When reduced with hydrogen in the presence of platinum-black, it yields ethyl*cyclo*hexane, b. p. 129—130° (Sabatier and Senderens give 128—129°). (2) A resin-like *polymeride*, which yields an explosive *ozonide* (I).



Isoprene under similar conditions yields (1) dipentene. (2) A *hydrocarbon*, b. p. 44°/9 mm., 160—161°/760 mm., D_0^{20} 0·8331, for which the formula $CMe\leqslant\begin{matrix}CH_2\cdot CH_2\\CH—CH_2\end{matrix}>CMe\cdot CH{:}CH_2$ is proposed; when reduced, it yields a *hydrocarbon*, $C_{10}H_{20}$, b. p. 164—165°/764 mm., D_0^{20} 0·799. (3) A resin-like *polymeride*, the *ozonide* of which has the constitution (II).



Di-isoprene yields the *hydrocarbon*,

$$CMe\leqslant\begin{matrix}CH—CH_2\\CMe\cdot CH_2\end{matrix}>CMe\cdot CMe{:}CH_2,$$

b. p. 85°/13 mm., D_0^{20} 0·8598, and a resin-like *polymeride*, which yields the *ozonide* (III). Z. K.

Isomorphous Mixtures of Para-dihalogen Derivatives of Benzene. NICOLAI N. NAGORNOFF (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 1159—1167).—1 : 4-Dichloro- and 1 : 4-di-iodo-benzene do not form solid solutions; their melting-point curve consists of two branches, with the eutectic point at 45° at the composition of 1·4 mol.% of the iodo-compound.

1 : 4-Dichloro- and 1 : 4-chloroiodo-benzene (m. p. 53°) form continuous isomorphous mixtures; their fusion curve passes through a minimum at 41° at the composition 50 mol.% of each compound.

1 : 4-Di-iodo- and 1 : 4-chloroiodo-benzene form solid solutions in one another. The saturated solution in chloroiodobenzene contains 20 mol.% of di-iodobenzene, whilst the saturated solution in the latter contains 15% of chloroiodobenzene. The curve consists of two branches, the eutetic point lying at 59° at the composition 14 mol.% of di-iodobenzene.

1 : 4-Dibromo- and 1 : 4-bromoiodo-benzene (m. p. 89·9°) form a continuous series of isomorphous mixtures; the minimum of their fusion curve is at 85·1°, corresponding with the composition of 60 mol.% of the dibromide.

1 : 4-Di-iodo- and 1 : 4-bromoiodo-benzene also form a continuous series of isomorphous mixtures, their curve passing through a minimum at about 100·5° at about 30 mol.% of di-iodo-benzene. Curves and tables are given for every pair of substances mentioned. Z. K.

Iodine Derivatives of Toluene. HENRY L. WHEELER (*Amer. Chem. J.*, 1910, **44**, 493—507).—In papers on the action of iodine on *o*-, *m*-, and *p*-toluidines (Abstr., 1910, i, 17, 19, 662), an account has been given of 2 : 3-, 3 : 5-, and 2 : 5-di-iodotoluenes, 3 : 4 : 5-, 2 : 3 : 6-, and 3 : 4 : 6-tri-iodotoluenes, and 2 : 3 : 4 : 6-tetraiodotoluene. The study of the iodotoluenes has now been continued.

[With CHARLES A. BRAUTLECHT.]—*5-Iodo-3-nitro-o-toluidine*, $NO_2 \cdot C_6H_2MeI \cdot NH_2$, m. p. 135°, prepared by the action of iodine chloride on 3-nitro-*o*-toluidine in presence of glacial acetic acid, forms orange needles. By the action of potassium iodide on the diazotisation product of this compound, *2 : 5-di-iodo-3-nitrotoluene*, $NO_2 \cdot C_6H_2MeI_2$, m. p. 95°, is obtained, which crystallises in colourless prisms, and on reduction with ferrous sulphate and ammonia is converted into *2 : 5-di-iodo-m-toluidine*, m. p. 82°, which forms pale brown prisms. When this substance is diazotised and the product treated with potassium iodide, 3 : 5 : 6-tri-iodotoluene is produced. *2 : 5-Di-iodoaceto-m-toluidide*, $C_6H_2MeI_2 \cdot NHAc$, m. p. 198—199°, forms long, colourless needles. When a mixture of 2 : 5-di-iodo-*m*-toluidine and iodine with ether, water, and calcium carbonate is warmed for eighteen hours, *2 : 5 : 6-tri-iodo-m-toluidine*, m. p. 119—120°, and 2 : 4 : 5 : 6-tetraiodo-*m*-toluidine are produced; the former crystallises in colourless needles, and when its diazotisation

product is treated with potassium iodide, 2 : 3 : 5 : 6-*tetraiodotoluene*, m. p. 125°, is obtained, which forms colourless needles.

4 : 5-*Di-iodo-o-toluidine*, $NH_2 \cdot C_6H_2MeI_2$, m. p. 85°, prepared by the action of iodine or iodine chloride on *p*-iodo-*o*-toluidine, forms stout needles or long prisms. When its diazotisation product is treated with potassium iodide, 3 : 4 : 6-tri-iodotoluene (Abstr., 1910, i, 663) is obtained. 5-*Iodo*-4-*nitro-o-toluidine*, m. p. 109°, prepared by the action of iodine chloride on *p*-nitro-*o*-toluidine, forms long, bright yellow prisms. When its diazotisation product is treated with potassium iodide, 2 : 5-*di-iodo*-4-*nitrotoluene*, m. p. 117°, is obtained, which crystallises in buff-coloured, prismatic plates. This compound, on reduction with ferrous sulphate and ammonia, yields 2 : 5-*di-iodo*-*p*-*toluidine*, m. p. 109°, which forms buff-coloured prisms, and when diazotised and treated with potassium iodide is converted into 2 : 4 : 5-tri-iodotoluene, m. p. 118°, which is identical with the compound described by Neumann (Abstr., 1887, 573) as 2 : 4 : 6-tri-iodotoluene. 2 : 4 : 6-*Tri-iodotoluene*, m. p. 105°, prepared by the diazotisation of 2 : 4 : 6-tri-iodo-*m*-toluidine, crystallises in colourless needles.

[With Charles Hoffman.]—3-*Iodo*-5-*nitro-o-toluidine*, m. p. 173°, obtained by the action of iodine chloride on 5-nitro-*o*-toluidine in presence of glacial acetic acid, forms long, brown prisms. By the action of potassium iodide on the diazotisation product of this compound, 2 : 3-*di-iodo*-5-*nitrotoluene*, m. p. 143°, is produced, which crystallises in long, light brown, prismatic needles, and when reduced with ferrous sulphate and ammonia is converted into 5 : 6-*di-iodo*-*m*-*toluidine*, m. p. 106°, which forms large, brown crystals, but can be obtained in a colourless condition by distillation with steam. 5 : 6-*Di-iodo*-m-*acetotoluidide* has m. p. 208°. 3 : 5 : 6-*Tri-iodotoluene*, m. p. 72—73°, obtained by the action of potassium iodide on the diazotisation product of 5 : 6-di-iodo-*m*-toluidine, forms large, pale orange plates. On warming a mixture of 5 : 6-di-iodo-*m*-toluidine with iodine for several hours in presence of water, ether, and calcium carbonate, 4 : 5 : 6-*tri-iodo*-m-*toluidine*, m. p. 122°, and 2 : 4 : 5 : 6-*tetra-iodo*-m-*toluidine*, m. p. 205°, are produced, which crystallise in small needles. 4 : 5 : 6-*Tri-iodo*-m-*acetotoluidide*, m. p. 265° (decomp.), forms colourless needles. 2 : 3 : 4-*Tri-iodotoluene*, m. p. 92°, obtained by the diazotisation of 4 : 5 : 6-tri-iodo-*m*-toluidine, forms radiating crystals. By the action of potassium iodide on the diazotisation product of 4 : 5 : 6-tri-iodo-*m*-toluidine, 3 : 4 : 5 : 6-*tetraiodotoluene*, m. p. 284—285°, is obtained, which crystallises in straw-coloured needles. *Pentaiodotoluene*, m. p. 340° (decomp.), obtained by the action of potassium iodide on the diazotisation product of 2 : 4 : 5 : 6-tetraiodo-*m*-toluidine, forms small, dull yellow needles. E. G.

Auto-decomposition of Phenylnitromethane. Friedrich Heim (*Ber.*, 1910, **43**, 3417—3420. Compare Dimroth, Abstr., 1910, i, 831).—In attempting to purify crude phenylnitromethane (Wislicenus and Endres, Abstr., 1902, i, 541) by distilling the crude product under diminished pressures, rapid decomposition ensued in one experiment, nitrous fumes were evolved, and a *product*, $C_{21}H_{17}ON$ (probably

triphenyldihydro*iso*oxazole), was obtained. This crystallises from alcohol, and has m. p. 138—139°. Other products were also formed.

In a second experiment, the crude product was subjected to steam distillation, and the phenylnitromethane obtained as a yellow oil; at the same time a small amount of a yellow solid was deposited in the condenser towards the end of the distillation, and dibenzhydroxamic acid was left in the flask.

Decomposition was also noticed when a specimen of phenylnitromethane, which has turned brown after exposure to light, was distilled.

It is suggested that the cause of the rapid decomposition is the presence of small amounts of phenylnitrolic acid in the crude material. J. J. S.

Nitro- and Amino-sulphobenzoic Acids. S. VAN DORSSEN (*Rec. trav. chim.*, 1910, [ii], **14**, 368—393).—In view of Taverne's statement (Abstr., 1906, i, 273) that *m*-sulphobenzoic acid on nitration furnishes 2-nitro-3-sulphobenzoic acid, whereas the symmetrical acid is to be expected, the author has re-investigated Taverne's acid and compared it with aminosulphobenzoic acids prepared in other ways. For the characterisation of the acids, the electrical conductivity and the solubility have been used. The results show that the acid prepared by Taverne is 3-nitro-5-sulphobenzoic acid. The conductivities quoted are for $v = 1200$ unless otherwise stated, and the solubilities are grams of acid in 100 grams of water, saturated at 25°.

4-Amino-2-sulphobenzoic acid, $\mu = 302{\cdot}4$, solubility 0·2997, crystallises in batons. 5-Amino-2-sulphobenzoic acid, $\mu = 332{\cdot}4$, solubility 0·1035, crystallises with $1H_2O$, and is unstable in aqueous solution. 4-Amino-3-sulphobenzoic acid, $\mu_{600} = 360{\cdot}0$, solubility 2·8346, was prepared by Fischer's method (Abstr., 1892, i, 331). Its constitution was established by the fact that aniline-*o*-sulphonic acid is formed with it as a by-product. 5-Nitro-3-sulphobenzoic acid, prepared from *m*-sulphobenzoic acid as described by Taverne, who wrongly assumed it to be the 2 : 3 isomeride, is identical with the acid prepared from *m*-nitrotoluene by sulphonation and subsequent oxidation of the CH_3– group, both acids furnishing *s*-dichlorobenzoic acid on treatment with phosphorus pentachloride. The nitro-acid, on reduction with tin and hydrochloric acid, furnishes the corresponding *amino-acid*, $\mu = 302{\cdot}4$, solubility 0·5745, and this gives no tribromoaniline with bromine water, a further proof of its symmetrical structure. 6-Amino-3-sulphobenzoic acid could not be obtained by sulphonating *o*-bromobenzoic acid and then replacing the bromine atom by $-NH_2$ by the action of ammonia, this reaction furnishing only aniline-*p*-sulphonic acid, $\mu_{128} = 93{\cdot}8$, which crystallises with 1 or 2 H_2O. 2-Amino-4-sulphobenzoic acid has $\mu = 356{\cdot}4$, solubility 1·0482, and shows a blue fluorescence in solution in water. 3-Amino-4-sulphobenzoic acid has $\mu_{1312} = 382{\cdot}9$, solubility 0·0810. Attempts to prepare 2-amino-3-sulphobenzoic and 2-amino-5-sulphobenzoic acids were unsuccessful. The sulphonation of *m*-aminobenzoic acid gives rise to a mixture of 3-amino-4-sulphobenzoic and 5-amino-2-sulphobenzoic acids (compare Griess, this Journ., 1872, 717)

These acids are all considerably ionised in solution, and, as in the case of the aminobenzenesulphonic acids, the ionisation decreases for the isomerides in the order ortho → para → meta (for the relative positions of $-HSO_3$ and $-NH_2$), whilst in the case of the aminobenzoic acids it diminishes in the order meta → ortho → para. The difference is probably due to the tendency to form internal salts in the ortho- and para-compounds in the first case. T. A. H.

Sulphonation of Benzenesulphonic Acid. JULIUS J. POLAK (*Rec. trav. chim.*, 1910, [ii], **14**, 416—446).—It is shown that in the sulphonation of benzenesulphonic acid, both meta- and para-disulphonic acids are formed, the former being the chief product. In sulphonating at high temperatures, some trisulphonic acid is produced.

Benzene-*o*-disulphonic acid was prepared from *o*-chloronitrobenzene by methods described by Blanksma (Abstr., 1900, i, 482) and by Wohlfahrt (Abstr., 1903, i, 203), the orthoanilic acid so obtained being converted into the *o*-disulphonic acid by Leuckart's method (Abstr., 1890, i, 603). The meta- and para isomerides were prepared by similar processes, but as regards the second of these, a better yield was obtained by Gattermann's process (Abstr., 1899, i, 516), starting from aniline-*p*-sulphonic acid. The method of determining the relative proportions of the two isomerides formed in the sulphonation of benzenesulphonic acid consisted in determining the solidifying point of the mixed sulphonyl chlorides, these being produced quantitatively by a special process from the potassium salts of the mixed acids. For this purpose it was necessary to construct a table showing the solidifying points of mixtures of the two pure sulphonyl chlorides, and this is given in the original. It shows a transition point for the para-isomeride at 71·6°.

The barium salt was used for sulphonation, as this could be obtained dry, and the temperature was controlled by conducting the experiments in vessels surrounded by vapours of substances boiling at the required temperatures.

Tables showing the relative percentages of the two disulphonic acids formed after various intervals, (*a*) with fuming sulphuric acid of known composition, (*b*) with 98% acid, that is, in presence of water, are given. At 183°, sulphonation is incomplete, whilst at 233° some trisulphonic acid is formed, but complete sulphonation to disulphonic acids takes place at 209°. It appears that meta- and para-acids are both formed initially, and that reciprocal transformation of both acids may then go on, the change para → meta being more rapid than the reverse one at 209°, but both are very slow, although they are accelerated by rise of temperature and by the presence of water. T. A. H.

Preparation of Certain Sulphonic Acids in the Free State. JOSEPH H. KASTLE (*Amer. Chem. J.*, 1910, **44**, 483—487).—A simple method is described for the preparation of certain sulphonic acids by precipitating them from concentrated aqueous solutions by the addition of another strong acid, such as hydrochloric or sulphuric acid.

p-Nitro-*o*-toluenesulphonic acid can be prepared in a pure state in the following manner. *p*-Nitrotoluene is treated with fuming sulphuric acid, and the product is poured into an equal volume of water.

On cooling, the sulphonic acid separates in crystals, and is collected, dissolved in a small quantity of water, precipitated by the addition of concentrated hydrochloric acid, and recrystallised several times from water. The acid is thus obtained in pale yellow prisms containing $2H_2O$, and not $2\frac{1}{2}H_2O$ as stated by Jenssen (Abstr., 1874, 479).

In a similar way, a toluenesulphonic acid, probably the para-compound, can be prepared, which forms colourless, prismatic crystals, containing $1H_2O$.

Attempts have been made to isolate benzenesulphonic and *o*-nitrotoluenesulphonic acids by this method, but without success. E. G.

Catalytic Reactions at High Temperatures. XXI. Influence of Foreign Substances on the Activity of Catalysts. Wladimir N. Ipatieff (*Ber.*, 1910, 43, 3387—3393).—Hydroaromatic compounds containing a double linking in the ring are completely reduced when heated with copper and hydrogen in an iron vessel, but when the vessel is of copper or phosphor-bronze, the reduction does not extend to this linking. Further experiments show that amylene is completely reduced at 300° in an iron tube in presence of copper oxide, but that no reduction occurs in the absence of the copper oxide, whilst in presence of copper or copper oxide, enclosed in a copper tube, the reduction is very incomplete, the reaction $C_5H_{10}+H_2 \rightleftarrows C_5H_{12}$ being reversible.

Using copper oxide in an iron tube, octahydronaphthalene is partly reduced to decahydronaphthalene, and partly decomposed, yielding *cyclo*hexane. The copper walls of the vessel may hinder the reaction, or it may be necessary that two catalysts should be simultaneously present. Further experiments are in progress. C. H. D.

Action of Metals on Aromatic Keto-chlorides and the Properties of Compounds of the Type $R_2CCl\cdot CClR_2$. James F. Norris, Ruth Thomas, and B. Marion Brown (*Ber.*, 1910, 43, 2940—2959. Compare Schmidlin and Escher, Abstr., 1910, i, 369).—In compounds of the type CR_2Cl_2, when the substituting radicle is positive or strongly negative, the halogen atom only reacts with difficulty with metals and certain metallic oxides; but on passing from the positive end of the series to the negative, the reactivity increases until keto-chlorides are obtained which readily part with chlorine. If the negative character of the substituting group is increased from this point, the compounds become stable again; for example, mercury only eliminates one halogen from benzophenone chloride, forming tetraphenylethylene dichloride; 4 : 4′-dichlorobenzophenone chloride and mercury yield a mixture of tetrachlorotetraphenylethylene and tetraphenylethylene; 2 : 4′-dichlorobenzophenone chloride gives exclusively tetrachlorotetraphenylethylene, whilst 2 : 5 : 2′ : 5′-tetrachlorobenzophenone chloride does not interact either with mercury or with zinc. Both zinc and silver act rapidly on benzophenone chloride, forming tetraphenylethylene.

Sulphuryl chloride in presence of small quantities of acetic acid was found to afford an effective means of causing the addition of chlorine to double linkings, and it is possible to obtain tetraphenylethylene

dichloride in this manner. This substance forms characteristic additive compounds with carbon tetrachloride and chloroform.

When tetraphenylethylene dichloride is slowly heated (compare Schmidlin and Escher, *loc. cit.*), the chief product is 4-chlorotetraphenylethylene. At higher temperatures, tetraphenylethylene is formed. With magnesium phenyl bromide, 4-phenyltetraphenylethylene is formed in addition to tetraphenylethylene.

Tetraphenylethylene dibromide could not be obtained by the action of metals on benzophenone bromide tetraphenylethylene being the sole product of the reaction. Tetraphenylethylene dichloride when heated with bromobenzene and sodium also yields tetraphenylethylene.

By the action of aluminium chloride on 4 : 4′ : 4″ : 4‴-tetrachlorotetraphenylethylene dichloride, 9 : 10-diphenylphenanthrene and a tetrachloro-substitution product are obtained; the para-hydrogen atoms take no part in the reaction.

Both triphenylmethyl and pentaphenylethane react with sulphuryl chloride, forming triphenylmethyl chloride in each instance; tetraphenylethane and sulphuryl chloride do not interact. Sulphuryl chloride converts triphenylcarbinol into triphenylmethyl chloride, and its trinitro-derivative into trinitrotriphenylmethyl chloride.

4 : 4′ : 4″ : 4‴-*Tetrachlorotetraphenylethylene* has m. p. 216—217°; the *dichloride* has m. p. 190—191°. Fluorenone chloride crystallises in long, straw-yellow needles, m. p. 101·5—102·5°. Silver converts it into bisdiphenylene ethylene; mercury into *dibiphenylene-ethylene dichloride*, which crystallises in colourless needles, m. p. 228—236°, to a red liquid.

4-*Phenylbenzophenone chloride* forms crystals, m. p. 45—47°. When boiled with diphenylmethane, 4-*phenyltetraphenylethylene* is formed, m. p. 189—190°. A *tetranitro*-derivative forms yellow crystals, m. p. 278—280°.

Convenient methods are described for the preparation of benzophenone, tetraphenylethylene, etc., on a large scale. E. F. A.

Gradual Synthesis of the Benzene Chain. Maurice Delacre (*Bull. Soc. chim.*, 1910, [iv], 7, 1041—1046. Compare Abstr., 1910, i, 120, 323).—A paper detailing the steps in the synthesis of triphenylbenzene from acetophenone, through dypnone, $CMePh{:}CHBz$, and dypnopinacone, $\begin{matrix}CH_2\cdot CPh{:}CH\cdot CPh\cdot OH\\ |\\ CH_2\cdot CPh{:}CH\cdot CPh\cdot OH\end{matrix}$. The latter, like the members of the homodypnopinacone and *iso*dypnopinacolin groups, furnishes readily the hydrocarbon, $C_{25}H_{22}$, the reduction product of which gives triphenylbenzene, allylbenzene, and ethylbenzene on heating. The remainder of the paper is devoted to discussing the bearing of this and other reactions among pinacolin derivatives, on the general question of the gradual synthesis of the benzene chain. T. A. H.

Bromo-salts of Platinum. Alexander Gutbier [with Fr. Bauriedel and C. J. Obermaier] *Ber.*, 1910, **43**, 3228—3234. Compare Abstr., 1910, i, 12).—Various substituted ammonium platinibromides have been prepared by adding a solution of the substituted

ammonium bromide to a solution of hydrogen platinibromide. The resulting precipitates were purified by recrystallisation from aqueous hydrobromic acid. In some cases there was a tendency for decomposition to take place when aqueous solutions were used, a resin being formed; this tendency could be obviated by using dilute alcoholic solutions of the substituted ammonium bromide and of hydrogen bromide.

Phenylammonium platinibromide, $(NH_3Ph)_2PtBr_6$: yellowish-red, felted crystals, which are still solid at 260°. *Phenylmethylammonium platinibromide*, $(NH_2MePh)_2PtBr_6$: bright red, rhombic needles, m. p. 227—228° (decomp.). *Phenyldimethylammonium platinibromide*, $(NHMe_2Ph)_2PtBr_6$: red needles. *Phenylethylammonium platinibromide*, $(NH_2EtPh)_2PtBr_6$: bright red, microscopic needles, m. p. 209—210°. *Phenyldiethylammonium platinibromide*, $(NHEt_2Ph)_2PtBr_6$: bright red, prismatic crystals. o-*Tolylammonium platinibromide*, $(NH_3{\cdot}C_6H_4Me)_2PtBr_6$: bright yellowish-red needles, probably monoclinic, m. p. 225—226° (decomp.). m-*Tolylammonium platinibromide*, $(NH_3{\cdot}C_6H_4Me)_2PtBr_6$: bright red, shining crystals, m. p. 266° (decomp.). p-*Tolylammonium platinibromide*, $(C_6H_4Me{\cdot}NH_3)_2PtBr_6$: shining, yellowish-red, flat prisms, m. p. 268—269°. 1:2:4-*Xylylammonium platinibromide*, $(C_6H_3Me_2{\cdot}NH_3)_2PtBr_6$: bright red, felted, rhombic needles, m. p. 262—263°. 1:3:4-*Xylylammonium platinibromide*: yellowish-red needles and plates, m. p. 256°. 1:4:5-*Xylylammonium platinibromide*: red, monoclinic needles or rhombic plates, m. p. 241°. *Pyridinium platinibromide*, $(PyH)_2PtBr_6$: shining, reddish-brown needles, which are still solid at 270°. α-*Picolinium platinibromide*, $(C_5NH_5Me)_2PtBr_6$: red or reddish-brown, rhombic plates, m. p. 211—212°. *Quinolinium platinibromide*, $(C_9NH_8)_2PtBr_6$: bright red, monoclinic prisms, m. p. 254—255° (decomp.). *Benzylammonium platinibromide*. $(NH_3{\cdot}C_7H_7)_2PtBr_6$: yellowish-red, rhombic plates, m. p. 257—259° (decomp.). *Benzylethylammonium platinibromide*, $(NH_2Et{\cdot}C_7H_7)_2PtBr_6$: bright red plates and needles, m. p. 177°. *Benzidinium platinibromide*, $[N_2H_6(C_6H_4)_2]PtBr_6$: yellowish-red monoclinic, needles, which are strongly pleochroic. o-*Phenylenediammonium platinibromide*, $[C_6H_4(NH_3)_2]PtBr_6$, brownish-yellow, monoclinic, pleochroic needles or plates. m-*Phenylenediammonium platinibromide*: dark red, rhombic needles, which do not melt at 270°. p-*Phenylenediammonium platinibromide*: dark red, monoclinic prisms, slightly pleochroic. α-*Naphthylammonium platinibromide*, $(C_{10}H_7{\cdot}NH_3)_2PtBr_6$: red, monoclinic crystals, which do not melt at 270°. β-*Naphthylammonium platinibromide*, reddish-yellow plates and prisms, which are still solid at 275°.

The above compounds are only very slightly soluble in cold water, giving yellow solutions; they are more soluble in hot water to yellowish-red or red solutions. T. S. P.

Hydroxy- and Dihydroxy-phenylalkylammonium Compounds, and β-Nitrostyrenes. KARL W. ROSENMUND (*Ber.*, 1910, **43**, 3412—3417).—Attempts have been made to synthesise compounds analogous to hordenine alkylhalides (compare Abstr., 1910, i, 241), the method of procedure consisting in the complete methylation of the alkyl ethers of the base, and then removal of the alkyl group of the phenolic ether by means of hydriodic acid. p-*Methoxyphenylisopropyltrimethylammonium iodide*,

$$OMe\cdot C_6H_4\cdot CH_2\cdot CHMe\cdot NMe_3I,$$

obtained by methylating *p*-methoxyphenyl*iso*propylamine, crystallises from water in long, colourless needles, m. p. 215—216°, and when boiled with hydriodic acid yields p-*hydroxyphenylisopropyltrimethylammonium iodide* in the form of colourless needles, m. p. 241—242°. 3 : 4-*Dimethoxyphenylisopropyltrimethylammonium iodide*,

$$C_6H_3(OMe)_2\cdot CH_2\cdot CHMe\cdot NMe_3I,$$

forms colourless crystals, m. p. 187°, and the corresponding *dihydroxy*-derivative crystallises from alcohol in colourless, compact prisms, m. p. 190°, and its aqueous solution gives the catechol reaction with ferric chloride.

A good yield of β-nitromethylenedioxystyrene (Bouveault and Wahl, *Bull. Soc. chim.*, 1903, [iii], **29**, 523; Medinger, *Monatsh.*, 1906, **27**, 244) is obtained by the gradual addition of a methyl-alcoholic solution of potassium hydroxide (1·5 mols.) to an alcoholic solution of piperonal and nitromethane, and then pouring the whole into an excess of ice-cold 10% hydrochloric acid. When reduced with zinc dust and a mixture of alcohol and glacial acetic acid, the nitro-compound yields homopiperonylaldoxime, m. p. 119—120°, and this when reduced with 3% sodium amalgam yields homopiperonylamine, the hydrochloride of which has m. p. 208° (Medinger, Abstr., 1906, i, 421, gives 197°).

β-Nitrodimethoxystyrene, $C_6H_3(OMe)_2\cdot CH{:}CH\cdot NO_2$, obtained from veratraldehyde and nitromethane, crystallises in yellow plates, m. p. 140°.

Veratraldehyde is easily prepared by methylating vanillin with methyl sulphate at 65—70° in the presence of 10% aqueous potassium hydroxide solution (compare Perkin and Robinson, Trans., 1907, **91**, 1079; Decker and Koch, Abstr., 1908, i, 35). J. J. S.

Action of Cyanogen Bromide on Tertiary Bases containing the Phenylethyl and Phenylpropyl Groups. JULIUS VON BRAUN (*Ber.*, 1910, **43**, 3209—3220. Compare Abstr., 1910, i, 189, 506).—It has been shown previously that groups containing an unsaturated linking in the βγ-position are, in general, more readily removed from amines by the action of cyanogen bromide than saturated groups. In order to ascertain if a similar influence is to be observed in the case of groups containing unsaturated linkings in more remote positions, the author has investigated the behaviour towards cyanogen bromide of tertiary amines of the following types: $CH_2Ph\cdot CH_2\cdot NR_2$ and $CH_2Ph\cdot CH_2\cdot CH_2\cdot NR_2$, and finds that the groups are more firmly attached as the length of the aliphatic chain increases.

Di-β-phenylethyl-dimethylammonium bromide,

$$NMe_2(CH_2{\cdot}CH_2Ph)_2Br,$$

soft, fatty leaflets, m. p. 160°, is obtained together with β-phenylethyldimethylamine, $NMe_2{\cdot}CH_2{\cdot}CH_2Ph$, b. p. 205°/760 mm. (compare Barger, Trans., 1909, **95**, 2193), by the action of β-phenylethyl bromide on dimethylamine.

Cyanogen bromide reacts vigorously with β-phenylethyldimethylamine, yielding *β-phenylethyltrimethylammonium bromide*,

$$CH_2Ph{\cdot}CH_2{\cdot}NMe_3Br,$$

m. p. 220°, β-phenylethyl bromide, and *β-phenylethylmethylcyanamide*, $CH_2Ph{\cdot}CH_2{\cdot}NMe{\cdot}CN$. The latter has b. p. 164—165°/10 mm., and is hydrolysed by sulphuric acid in aqueous alcoholic solution to *as*-β-phenylethylmethylcarbamide, $C_2H_4Ph{\cdot}NMe{\cdot}CO{\cdot}NH_2$; energetic hydrolysis yields β-phenylethylmethylamine, $NHMe{\cdot}C_2H_4Ph$ (compare Johnson and Guest, Abstr., 1909, i, 794).

Phenyl-β-phenylethylmethylamine, $NMePh{\cdot}C_2H_4Ph$, obtained from β-phenylethyl bromide and methylaniline, is a pale yellow liquid, b. p. 198—199°/18 mm., and solidifies in ice to a snow-white mass, m. p. 44°; it yields a *picrate*, m. p. 101°, and a *platinichloride*, m. p. 162—163° (decomp.); when treated with cyanogen bromide, it yields *β-phenylethylphenylcyanamide*, $C_2H_4Ph{\cdot}NPh{\cdot}CN$, b. p. 220—225°/11 mm. (slight decomp.), together with methyl bromide and β-phenylethyl bromide.

β-Phenylethyldiethylamine, $NEt_2{\cdot}C_2H_4Ph$, prepared by heating β-phenylethyl bromide with diethylamine, is a colourless, almost odourless liquid, b. p. 103°/10 mm., and gives a crystalline *picrate*, m. p. 95°, and an oily *platinichloride*, which slowly solidifies, m. p. 140°; when heated with cyanogen bromide, it yields β-phenylethyl bromide and *β-phenylethylethylcyanamide*, $C_2H_4Ph{\cdot}NEt{\cdot}CN$, which has b. p. 174°/15 mm., and is hydrolysed by sulphuric acid to *β-phenylethylethylamine*, $NHEt{\cdot}C_2H_4Ph$, a colourless oil, b. p. 99—100°/13 mm.; the latter gives an oily *platinichloride*, which slowly solidifies, and a crystalline *picrate*, m. p. 130°, a *phenylthiocarbamide*, $C_2H_4Ph{\cdot}NEt{\cdot}CS{\cdot}NHPh$, m. p. 88°, and a *carbamide*,

$$C_2H_4Ph{\cdot}NEt{\cdot}CO{\cdot}NH_2,$$

m. p. 58°; the *benzoyl* and *benzenesulphonyl* derivatives are oils.

γ-Phenylpropyldimethylamine (Senfter and Tafel, Abstr., 1894, i, 579) is obtained by the interaction of γ-phenylpropyl chloride or bromide with dimethylamine.

The action takes place more readily with the bromide, but is accompanied by the formation of an oily quaternary *bromide*,

$$NMe_2(C_3H_6Ph)_2Br,$$

which is converted by silver chloride into the corresponding *chloride*, m. p. 88°.

γ-Phenylpropyldimethylamine reacts vigorously with cyanogen bromide, yielding γ-phenylpropylmethylcyanamide and *γ-phenylpropyltrimethylammonium bromide*, $CH_2Ph{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3Br$, which forms a red, crystalline *platinichloride*, m. p. 205—209°.

γ-Phenylpropylmethylcyanamide, $C_3H_6Ph{\cdot}NMeCN$, b. p. 187—189°/17 mm., forms a colourless liquid, and is hydrolysed with difficulty. On heating for several hours at 170° with strong hydrochloric acid, it

is converted into *γ-phenylpropylmethylamine*, $NHMe{\cdot}C_3H_6Ph$, a colourless oil, b. p. 110°/17 mm., which gives an oily *picrate* and a crystalline *platinichloride*, m. p. 188°; the *carbamide*, $C_3H_6Ph{\cdot}NMe{\cdot}CO{\cdot}NH_2$, crystallises in leaflets, m. p. 101°.

The direct interaction of γ-phenylpropyl chloride or bromide and methylamine furnishes a very small yield of γ-phenylpropylmethylamine.

γ-Phenylpropyldiethylamine, $NEt_2{\cdot}C_3H_6Ph$, prepared from γ-phenylpropyl bromide and diethylamine, is a colourless liquid, b. p. 137—139° 22 mm., giving an oily *picrate* and *platinichloride*. It is converted by the action of cyanogen bromide into a mixture of γ-phenylpropyl bromide, diethylcyanamide, and *γ-phenylpropylethylcyanamide*,

$$C_3H_6Ph{\cdot}NEt{\cdot}CN.$$

The latter has b. p. 191—192°/14 mm., and is hydrolysed by hydrochloric acid into *γ-phenylpropylethylamine*, a colourless liquid, b. p. 118°/16 mm.

γ-Phenylpropyldipropylamine, $NPr^{\alpha}_2{\cdot}C_3H_6Ph$, obtained from γ-phenylpropyl bromide and dipropylamine, is a colourless, almost odourless liquid, b. p. 158—160°/17 mm.; the *picrate* is an oil; the *platinichloride* has m. p. 91—93°. It reacts vigorously with cyanogen bromide, yielding propyl bromide, γ-phenylpropyl bromide, and *γ-phenylpropylpropylcyanamide*, $C_3H_6Ph{\cdot}NPr^{\alpha}{\cdot}CN$, b. p. 200°/16 mm. The latter is hydrolysed by hydrochloric acid into *γ-phenylpropylpropylamine*, $NHPr^{\alpha}{\cdot}C_3H_6Ph$, a colourless, odourless liquid, b. p. 134°/17 mm., which forms an orange-yellow, crystalline *picrate*, m. p. 97°, and an oily *platinichloride*. F. B.

Isomerism of Anils (Schiff's Bases). III. Wilhelm Manchot (*Ber.*, 1910, 43, 3359—3362).—Reply to Anselmino (Abstr., 1910, i, 462), who has not appreciated the fact that the object of the molecular-weight determinations by Manchot and Furlong (Abstr., 1909, i, 805; 1910, i, 33) is to ascertain whether the entire differences between the two forms of an anil may not be due to differences in molecular magnitude. The existence of a temperature limit, stated by Anselmino, above and below which the two forms of an anil are stable respectively, is disproved by the fact that the yellow form of *p*-bromosalicylaldehydeanil separates from solutions at temperatures much higher than 33°, the limit set by Anselmino. C. S.

Sulphanilide. Alfred Wohl and Franz Koch (*Ber.*, 1910, 43, 3295—3307).—A good yield of sulphanilide (W. Traube, Abstr., 1891, 569) can be obtained by dropping a solution of sulphuryl chloride dissolved in dry ether into an excess of aniline dissolved in about three times its volume of dry ether and cooled by a good freezing mixture. The yield is 60% of the theoretical, and the by-product is azobenzene. When chloroform or carbon tetrachloride is used as diluent, Mohr's trianilinobenzene (Abstr., 1890, 614) is formed. The anilide is not readily hydrolysed, and is not affected when heated with sodium ethoxide at 180°.

The *disodium* salt, $C_{12}H_{10}O_2N_2SNa_2$, crystallises on the addition of

benzene and light petroleum to its alcoholic solution in slender, glistening needles containing alcohol. The *acetyl* derivative,

$$NPhAc\cdot SO_2\cdot NHPh,$$

prepared by the action of acetic anhydride and a little sulphuric acid at the ordinary temperature, forms compact, rhombic prisms, m. p. 158—159°, after sintering at 155°, and dissolves in alkalis. The *diacetyl* derivative, $SO_2(NAcPh)_2$, obtained by using a temperature of 45°, crystallises from carbon tetrachloride in prismatic needles, m. p. 164°, after sintering at 159°. This compound is decomposed readily when heated with acetic anhydride, yielding diacetanilide and sulphuric acid, but at the same time the sulphuric acid reacts with the acetylsulphonamic acid, which is an intermediate product, yielding acetylaniline-*p*-sulphonic acid:

$$SO_2(NPhAc)_2 \longrightarrow NPhAc\cdot SO_3H \longrightarrow NHAc\cdot C_6H_4\cdot SO_3H.$$

Diphenyldimethylsulphamide, $SO_2(NPhMe)_2$, obtained by the action of methyl iodide and sodium methoxide at 100°, crystallises in prismatic needles or plates, m. p. 96—97°, and is also formed when silver oxide and methyl iodide are used.

An explosive *dinitroso*-derivative, $SO_2(NPh\cdot NO)_2$, is formed when nitrous fumes are passed into a dry ethereal solution of the anilide. It forms hygroscopic crystals, which explode at 73—74°. Ethereal or chloroform solutions of the nitroso-derivative, and also of the nitroso-derivative of 4 : 4′-dibromosulphanilide, condense with β-naphthol, yielding azo-derivatives and black azo-dyes, which have not been obtained pure.

A solution of sulphanilide in sodium carbonate reacts with an excess of a diazotised solution of *p*-nitroaniline, yielding a brownish-black dye.

2 : 4 : 2′ : 4′-*Tetranitrodiphenylsulphamide*, $SO_2[NH\cdot C_6H_3(NO_2)_2]_2$, prepared by adding the sulphamide or, still better, its mono- or diacetyl derivative to fuming nitric acid cooled to 0°, separates as well developed prisms, m. p. 183°, and is decomposed when boiled with water. Fuming nitric acid reacts with a well cooled sulphuric acid solution of the anilide, yielding *o*-nitroaniline-*p*-sulphonic acid. A chloroform solution of bromine converts the anilide into its 4 : 4′-*dibromo*-derivative, $C_{12}H_{10}O_2N_2Br_2S$, in the form of plates, m. p. 124—125°. The bromo-derivative reacts with sodium acetate and acetic anhydride, yielding *p*-bromoacetanilide. When further brominated, the dibromo-derivative yields 2 : 4 : 4′-*tribromodiphenylsulphamide*, $C_{12}H_9O_2N_2Br_3S$, which crystallises from benzene in tetragonal pyramids, m. p. 143°.

Sulpho-p-toluidide, $C_{14}H_{16}O_2N_2S$, obtained when a chloroform solution of sulphonyl chloride is added to a well cooled solution of *p*-toluidine in dry chloroform, crystallises from carbon tetrachloride or light petroleum in colourless, prismatic needles, m. p. 96—97°.

Nitroanilines, acetanilide, and aniline hydrochloride do not react with sulphuryl chloride, and monomethylaniline yields dark brown dyes. J. J. S.

Comparative Nitration of Mono- and Diacylated Aromatic Amines. Frédéric Reverdin and Armand de Luc (*Ber.*, 1910, 43, 3460—3464; *Compt. rend.*, 1910, 151, 985. Compare Abstr., 1909. i, 377, 913).—A comparative examination of the nitration of a few

acylated and diacylated aromatic amines has been undertaken in order to ascertain what influence is exerted on the stability of the molecule by the second acyl group attached to the nitrogen atom, and what orientating effect it has on the entrant nitro-group. The experimental results are given only in the paper in the *Berichte*.

As already recorded, 2 : 3-dinitro-4-toluenesulphonylaminoanisole is obtained when 1 part of 4-toluenesulphonylaminoanisole in 10 parts of glacial acetic acid is added to 5 parts of nitric acid, D 1·52, between 20—30°; under the same conditions, 4-acetyltoluenesulphonylaminoanisole is unchanged. When, however, using the same proportions, the temperature is allowed to rise to 60°, the first substance behaves as before, whilst the diacylated compound yields 3-*nitro*-4-*acetyltoluenesulphonylaminoanisole*, $OMe\cdot C_6H_3(NO_2)\cdot NAc\cdot SO_2\cdot C_7H_7$, m. p. 197°. Finally, when the monoacylated compound is added to the nitric acid below 20°, and the mixture, after being heated momentarily to 55°, is poured into water, the 2 : 3-dinitro-compound is obtained, together with the 3-nitro-compound. Under the same conditions (except that the temperature can be raised to 65° before gas is evolved), the diacylated compound yields 2 : 5-*dinitro*-4-*acetyltoluenesulphonylaminoanisole*, m. p. 169°, yellow leaflets, and the 2 : 3-dinitro-*isomeride*, m. p. 205°, colourless needles, which are soparated by the greater solubility of the former in hot alcohol.

3-Nitroaceto-*p*-toluidide is formed when aceto-*p*-toluidide in acetic acid is added to nitric acid below 15° and the temperature is then raised gradually to 65°; the same compound is also formed when diaceto-*p*-toluidide is treated similarly, the temperature being raised, however, only to 20° (evolution of gas). When nitrated by nitric acid alone, aceto-*p*-toluidide at 65° (evolution of gas) yields 38% of 3 : 5-dinitroaceto-*p*-toluidide and 62% of 3-nitroaceto-*p*-toluidide, whilst diaceto-*p*-toluidide must be cooled by ice during the nitration, and yields 3-nitro-*p*-toluidine.

When nitrated in acetic acid solution, 4-toluenesulphonylaminotoluene at 70° yields 80% of 3 : 5-*dinitro*-4-*toluenesulphonylaminotoluene*, $C_6H_2Me(NO_2)_2\cdot NH\cdot SO_2\cdot C_7H_7$, m. p. 204° (the same substance is also produced at 40° in the absence of the acetic acid), whilst 4-*acetyltoluenesulphonylaminotoluene*, $C_6H_4Me\cdot NAc\cdot SO_2\cdot C_7H_7$, m. p. 134°, obtained from 4-toluenesulphonylaminotoluene and acetic anhydride, is not nitrated, even at 75°; when, however, the diacylated compound is treated below 15° with nitric acid alone, the temperature being raised subsequently to 40° (evolution of gas), 2-*nitro*-4-*nitrotoluenesulphonylaminotoluene*, $NO_2\cdot C_6H_3Me\cdot NH\cdot SO_2\cdot C_7H_6\cdot NO_2$, m. p. 183°, is obtained, which yields 2-nitro-*p*-toluidine by hydrolysis.

From the preceding experiments, it seems that the presence of the acetyl and the toluenesulphonyl groups increases the stability of the molecule, and, in the case of *p*-toluidine, affects the orientation of the nitro-group and facilitates the introduction of a nitro-group into the toluenesulphonyl nucleus; the presence of two acetyl groups in *p*-toluidine apparently diminishes the stability of the molecule. C. S.

Action of Phenylthiocarbimide on Mono- and Di-*iso*amylaniline. THEODOR ST. WARUNIS (*Ber.*, 1910, **43**, 2972—2976).—By the

action of phenylthiocarbimide on mono*iso*amylaniline, *diphenyliso*amyl*thiocarbamide*, $NHPh{\cdot}CS{\cdot}NPh{\cdot}C_5H_{11}$, is formed; the same compound is obtained from crude di*iso*amylaniline, owing to the mono-derivative present as impurity. It crystallises in large, transparent, colourless needles, m. p. 107·5°, and sublimes at 240—250°.

To determine sulphur in organic substances, they are heated with a mixture of potassium hydroxide and sodium peroxide in a silver crucible, at first at 75—85°, and subsequently over a small flame.

E. F. A.

Some Derivatives of 3 : 4 : 5-Trinitro-2-methoxytoluene. Jan J. Blanksma (*Rec. trav. chim.*, 1910, **29**, 410—415).—The 3 : 4 : 5-trinitro-2-methoxytoluene was prepared by the nitration of 4-nitro-2-methoxytoluene (Kaufler and Wenzel, Abstr., 1901, i, 590). When treated with ammonia, it yields chiefly 3 : 5-*dinitro*-2-*methoxy*-p-*toluidine* as yellow crystals, m. p. 130°, the *acetyl* derivative of which melts at 220°.

By the diazotisation of 3 : 5-dinitro-2-methoxy-*p*-toluidine, colourless crystals of 3 : 5-dinitro-2-methoxytoluene are produced; when treated with ammonia, this is transformed into 3 : 5-dinitro-*o*-toluidine. On heating 3 : 4 : 5-trinitro-2-methoxytoluene with ammonia in a sealed tube, dark brown crystals of 3 : 5-dinitro-2 : 4-tolylenediamine, m. p. 254°, are formed; Nietzki and Rösel found 300° as the melting point of this substance (Abstr., 1891, 192); its *acetyl* derivative does not melt below 300°.

3 : 5-*Dinitro*-2 : 4-*di*(*methylnitroamino*)*toluene* forms colourless crystals, m. p. 169°; 2-*chloro*-5-*nitro*-4-*aceto*-p-*toluidide* crystallises in pale yellow crystals, m. p. 112°.

N. C.

Quinol Di*iso*butyl Ether. Rudolf Nietzki and Kesselring (*Ber.*, 1910, **43**, 3459—3460).—Attempts to prepare Schubert's tetranitroquinol di*iso*butyl ether (Abstr., 1883, 60) have resulted in the preparation of only a *trinitro*-compound, $C_{14}H_{19}O_8N_3$, m. p. 96°, even when fuming nitric acid and high temperatures have been employed.

C. S.

Phenols Insoluble in Alkalis. Henry A. Torrey and Roger Adams (*Ber.*, 1910, **43**, 3227—3228. Compare Abstr., 1907, i, 325; 1908, i, 460).—Of the isomeric nitrophenylhydrazones of paenol and bromopaenol, only the para-compounds are soluble in aqueous sodium hydroxide.

Paenol-o-nitrophenylhydrazone,

$$OH{\cdot}C_6H_3(OMe){\cdot}CMe{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2,$$

crystallises in deep red, monoclinic prisms, m. p. 217°; the m-*nitro*-derivative in red lamellæ, m. p. 197°, and the p-*nitro*-derivative in red crystals, m. p. 235—236° (decomp.).

Bromopaenol-o-nitrophenylhydrazone forms red needles, m. p. 253—254°; the m-*nitrophenylhydrazone*, brownish-red lamellæ, m. p. 208°, and the p-*nitro*-derivative, orange needles, m. p. 222°.

F. B.

***p*-Aminothiophenol [*p*-Aminophenyl Mercaptan].** II. Theodor Zincke and P. Jörg (*Ber.*, 1910, **43**, 3443—3450. Compare Abstr., 1909, i, 789).—*p*-Methylthiolaniline (*p*-aminophenyl methyl sulphide)

resembles aniline in many of its reactions, for example, it reacts with quinones, yielding intensely coloured anilino-derivatives, it condenses with 1-chloro-2 : 4-dinitrobenzene, yielding a substituted diphenylamine derivative, and yields diazonium salts which are readily transformed into corresponding chloro- and cyano-derivatives.

Dimethylthiolanilino-p-*benzoquinone*, $C_6H_2O_2(NH\cdot C_6H_4\cdot SMe)_2$, prepared by boiling an alcoholic solution of the aminothiophenol with *p*-benzoquinone for a short time, separates from tetrachloroethane as a finely crystalline powder, and dissolves in concentrated sulphuric acid to a deep bluish-green solution. The *derivative* from α-naphthaquinone, $C_6H_4<\begin{matrix}CO\cdot CH\cdot NH\cdot C_6H_4\cdot SMe\\ \|\\ CO\cdot CH\end{matrix}$, crystallises from hot alcohol in dark red, glistening plates with a metallic lustre, and has m. p. 164—165°; when boiled with alkalis it is slowly decomposed, and yields hydroxynaphthaquinone. The isomeric *compound* from β-naphthaquinone, $C_6H_4<\begin{matrix}CO-C(OH)=CH\\ C(:N\cdot C_6H_4\cdot SMe)\end{matrix}>$, crystallises from a mixture of alcohol and glacial acetic acid in brownish-red plates, and needles with a golden-yellow lustre, and has m. p. 242—243°. Its solution in concentrated sulphuric acid has a brownish-violet colour. It is more stable than the corresponding dianilino-derivative of β-naphthaquinone, and is not transformed so readily into derivatives of α-naphthaquinone.

2 : 4-*Dinitro*-4′-*methylthioldiphenylamine*, $C_6H_3(NO_2)_2\cdot NH\cdot C_6H_4\cdot SMe$, prepared by boiling an alcoholic solution of the *p*-methylthiolaniline and 1-chloro-2 : 4-dinitrobenzene with potassium acetate, crystallises from glacial acetic acid in dark orange-red needles or stout plates, m. p. 141°, and when reduced with an aqueous alcoholic solution of sodium sulphide yields 4-*nitro*-2-*amino*-4′-*methylthioldiphenylamine*, $NO_2\cdot C_6H_3(NH_2)\cdot NH\cdot C_6H_4\cdot SMe$, which crystallises from alcohol in dark reddish-brown needles or plates, m. p. 128°. Its solution in concentrated sulphuric acid has a deep bluish-green colour.

The diazonium chloride from *p*-methylthiolaniline couples with an alkaline solution of β-naphthol, yielding a deep red *azo-dye*. The *diazoamino*-compound, $SMe\cdot C_6H_4\cdot N:N\cdot NH\cdot C_6H_4\cdot SMe$, crystallises from light petroleum in pale brown needles, m. p. 99°. p-*Methylthiolbenzonitrile*, $CN\cdot C_6H_4\cdot SMe$, crystallises from dilute methyl alcohol in colourless plates, m. p. 64°, and on hydrolysis yields p-*methylthiolbenzoic acid*, $SMe\cdot C_6H_4\cdot CO_2H$, which crystallises in colourless, flat needles, m. p. 192°. 1-*Methylthiol*-4-*iodobenzene*, $C_6H_4I\cdot SMe$, crystallises in colourless plates, m. p. 38°; the *dibromide*, $C_6H_4I\cdot SBr_2Me$, crystallises in dark garnet-red needles, and with water yields the *sulphoxide*, $C_6H_4I\cdot SOMe$, which crystallises from light petroleum in needles, m. p. 112°. The *iododichloride*, $ICl_2\cdot C_6H_4\cdot S\cdot CCl_3$, prepared by the action of chlorine on a chloroform solution of the iodo-derivative in the absence of all traces of moisture, crystallises in pale yellow needles, and by the removal of chlorine yields p-*iodophenyl trichloromethyl sulphide*, $C_6H_4I\cdot S\cdot CCl_3$, which crystallises from light petroleum in colourless needles, m. p. 103°. Aniline reacts with the trichloro-derivative, yielding triphenylguanidine and *iodophenyl mercaptan*, $C_6H_4I\cdot SH$, the latter of which crystallises in nacreous plates, m. p. 85°. Other

methylthiols react in a similar manner. p-*Nitrophenyl trichloromethyl sulphide*, $NO_2 \cdot C_6H_4 \cdot S \cdot CCl_3$, has m. p. 94°. *Acetylaminochlorophenyl trichloromethyl sulphide*, $NHAc \cdot C_6H_3Cl \cdot S \cdot CCl_3$, crystallises in plates, m. p. 136°. It reacts with aniline, yielding triphenylguanidine and acetylaminochlorophenyl mercaptan, the *disulphide* of which has m. p. 181°.

When the *p*-iodophenyl methyl sulphide is treated with chlorine in chloroform solution, and then exposed to the air and shaken with potassium iodide solution, Langmuir's *p*-iodobenzenesulphonyl chloride (Abstr., 1895, i, 230) is obtained. The corresponding *anilide*, $C_{12}H_{10}O_2NSI$, forms colourless, fibrous needles, m. p. 143°.

J. J. S.

Action of Bromine on Diphenyl Sulphide, Diphenyl Sulphoxide, and Diphenylsulphone. Jacob Böeseken (*Rec. trav. chim.*, 1910, **29**, 315—329).—Bromine reacts with diphenyl sulphide to give a mixture of 4-bromodiphenyl sulphide and 4 : 4′-dibromodiphenyl sulphide. With chlorine in glacial acetic acid solution, 4 : 4′-dichlorodiphenyl sulphide is produced, but with dilute acetic acid only the sulphone. In the case of diphenylsulphoxide, a direct replacement by bromine does not take place, but in the presence of a little hydrobromic acid, 4 : 4′-dibromodiphenyl sulphide is formed, as in the case of the sulphide; no corresponding chloroderivative is produced by the action of chlorine. Bromine does not react easily with diphenylsulphone, but at high temperatures the molecule is broken up with the formation of sulphuryl bromide and bromobenzene; a similar change is brought about by the action of chlorine.

N. C.

Electrolytic Oxidation of Aromatic Sulphides. Fritz Fichter and Ph. Sjöstedt (*Ber.*, 1910, **43**, 3422—3429).—The electrolytic oxidation of benzyl sulphide gives three different products according to the conditions. In all cases the benzyl sulphide is dissolved in glacial acetic acid and a platinum anode used; a divided cell is unnecessary, since the products of reaction are only reduced with difficulty at a platinum cathode. If concentrated hydrochloric acid is added to the glacial acetic acid solution, and electrolysis carried out at 25°, using 0·08 ampere per sq. cm., and passing slightly less than the theoretical current, an almost theoretical yield of benzyl sulphoxide is obtained. Excess of current should be avoided, or else benzaldehyde is formed. Benzyl sulphide dichloride is probably first formed, and this is then hydrolysed into benzylsulphoxide and hydrogen chloride. Oxygen acids in place of hydrochloric acid give rise to further oxidation products of benzyl sulphide.

When the oxidation is carried out in hydrochloric-acetic acid solution at 90—95°, benzyldisulphoxide is formed. The benzylsulphoxide first formed is decomposed by the hydrochloric acid, the chief product being benzyldisulphide (compare Smythe, Trans., 1909, **95**, 349); the benzyl disulphide is then oxidised to the disulphoxide. Special experiments proved that benzyldisulphoxide is readily obtained by the electrolytic oxidation of benzyl disulphide.

When sulphuric acid is added to the acetic acid instead of hydrochloric acid, and the electrolysis carried out at 18°, *tribenzylsulphinium sulphate*, $(C_7H_7)_3S\cdot SO_4H$, is formed. The benzyl sulphide is oxidised to a mixture of benzyl alcohol and benzylsulphinic acid,

$$(C_7H_7)_2S + 2O + H_2O = C_7H_7\cdot OH + C_7H_7\cdot SO_2H,$$

and the former compound, in the presence of sulphuric acid, unites with the excess of benzyl sulphide, forming tribenzylsulphinium sulphate. This is proved by the ready formation of this compound by the interaction of benzyl sulphide and benzyl alcohol in sulphuric-glacial acetic acid solution at 70°. It is also formed by dissolving mono-tribenzylsulphinium ferrichloride in water, precipitation of the iron with ammonium hydroxide, and addition of ammonium sulphate and excess of sulphuric acid to the filtrate.

Tribenzylsulphinium sulphate forms cubes from alcohol, m. p. 170—175° (decomp.).

Replacement of hydrochloric and sulphuric acids by hydrobromic, hydrofluoric, nitric or phosphoric acids, addition of cerium salts as oxygen carriers, etc., did not give such good results in the electrolytic oxidation.

Dibenzylsulphone could not be prepared electrolytically either from benzyl sulphide or sulphoxide, but diphenylsulphone is readily obtained from phenyl sulphide at 20—30° in hydrochloric-glacial acetic acid solution. Diphenylsulphoxide prepared electrolytically is always mixed with unchanged phenyl sulphide and with diphenylsulphone. T. S. P.

Transformations of *cyclo*Butyldimethylcarbinol. IV. Nicolai M. Kijner (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1211—1227. Compare Abstr., 1908, i, 530, 864).—*cyclo*Butyldimethylcarbinol reacts with oxalic acid, yielding *cyclo*pentane derivatives and a crystalline isomeric alcohol of higher b. p., 1 : 1-*dimethylcyclopentan*-2-*ol*, $\begin{matrix}CH_2\cdot CMe_2\\ |\\ CH_2-\!-CH_2\end{matrix}\!\!>\!CH\cdot OH$, which, when oxidised with potassium permanganate or chromic acid, yields the corresponding pentanone (the semicarbazone of which has m. p. 191°) and αα-dimethylglutaric acid. 1 : 1-Dimethyl*cyclo*pentan-2-one,

$$\begin{matrix}CH_2\cdot CH_2\\ |\\ CH_2-\!-CO\end{matrix}\!\!>\!CMe_2,$$

has b. p. 143—143·5°/752 mm., D_0^{20} 0·8988, n_D^{20} 1·4343, and always gives some aldehydic reactions. When oxidised with potassium permanganate it yields: (1) *as*-dimethylsuccinic acid; (2) αα-dimethylglutaric acid, hexagonal plates, m. p. 83·5—84°, of which the *silver* salt, $C_7H_{10}O_4Ag_2$, and *aniline* salt, m. p. 144·5°, were prepared. The latter when boiled yields *dimethylglutaranil*, $CH_2<\begin{matrix}CMe_2\cdot CO\\ |\\ CH_2-\!-CO\end{matrix}\!\!>\!NPh$, hexagonal plates, m. p. 122—122·5°.

When treated with hydrazine hydrate, 1 : 1-dimethyl*cyclo*-

pentanone yields an *hydrazone*, $\begin{matrix}CH_2\cdot CMe_2\\ |\\ CH_2-CH_2\end{matrix}\!\!>C\!:\!N\cdot NH_2$, m. p. 20—24°, b. p. 101—104°/30 mm., D_0^{20} 0·9368, n_D^{20} 1·4859; it reduces ammoniacal silver solution, and is readily decomposed by water. With magnesium methyl iodide, the pentanone yields 1 : 1 : 2-trimethyl*cyclo*pentan-2-ol, b. p. 80—81°/49 mm., 156°/755 mm., D_0^{20} 0·9102, n_D^{20} 1·4513, which forms a crystalline *hydrate*, $(C_8H_{16}O),2H_2O$, m. p. 59—60°. Blanc's compound (*Compt. rend.*, 1906, **142**, 105), obtained similarly, was a hydrate and not the free pentanol. When distilled with oxalic acid, the trimethylpentanol yields 1 : 1 : 2-trimethyl*cyclo*pentene (*iso*laurolene),

$$\begin{matrix}CH\!:\!CMe\\ |\\ CH_2\cdot CH_2\end{matrix}\!\!>CMe_2,$$

b. p. 108·5—109°/754 mm., D_0^{15} 0·7868, D_{15}^{15} 0·7871, D_0^0 0·7824, n_D^{20} 1·4324, which with ammoniacal silver oxide solution yields a silver mirror, and when reduced with hydrogen iodide forms 1 : 1 : 2-trimethyl*cyclo*pentane, b. p. 113—114°/749 mm., D_{15}^{15} 0·7706, D_0^{20} 0·7661, n_D^{20} 1·4199.

In the formation of 1 : 1-dimethylpentanone by the oxidation of the pentanol, a volatile *acid*, $C_6H_{11}\cdot CO_2H$, is formed as a by-product; the *silver* salt was prepared. Z. K.

Diphenyl*cyclo*butylcarbinol and its Transformations. Nicolai M. Kijner (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1227—1236).—Diphenyl*cyclo*butylcarbinol, $CH_2\!<\!\begin{matrix}CH_2\\ CH_2\end{matrix}\!\!>CH\cdot CPh_2\cdot OH$, is obtained by the action of *cyclo*butanecarboxylic acid on magnesium phenyl iodide, diphenyl being found as a by-product. It forms regular, rhombohedral crystals, m. p. 54—54·5°, b. p. 198°/13 mm., D_9^{20} 1·0906, n_D^{20} 1·5882, and with hydrogen bromide yields a *bromide*, $C_{17}H_{17}Br$, m. p. 94·5—95°. When boiled with oxalic acid, it forms *diphenyl*cyclo*butylidenemethane*, $CH_2\!<\!\begin{matrix}CH_2\\ CH_2\end{matrix}\!\!>C\!:\!CPh_2$, m. p. 58°, which with chromic acid mixture is oxidised to benzophenone, whilst with nitric acid the unsaturated hydrocarbon decomposes into benzophenone and succinic acid. It dissolves in a saturated solution of hydrogen bromide in glacial acetic acid, forming a *bromide*, seemingly identical with the one obtained from diphenyl*cyclo*butylcarbinol, but with bromine in carbon disulphide solution, it forms a *dibromide*, $CH_2\!<\!\begin{matrix}CH_2\\ CH_2\end{matrix}\!\!>CBr\cdot CPh_2Br$, m. p. 91—92°, which when boiled with methyl alcohol forms *diphenyl-bromocyclobutylcarbinyl methyl ether*, $CH_2\!<\!\begin{matrix}CH_2\\ CH_2\end{matrix}\!\!>CBr\cdot CPh_2\cdot OMe$, m. p. 81—81·5°. When reduced with sodium ethoxide, diphenyl*cyclo*butylidenemethane forms either elongated plates or stout, hexagonal crystals of *diphenyl*cyclo*butylmethane*, $CH_2\!<\!\begin{matrix}CH_2\\ CH_2\end{matrix}\!\!>CH\cdot CHPh_2$, m. p. 39·5°, $D_{4^\circ}^{43\cdot5}$ 1·0003, $n_D^{43\cdot5}$ 1·5636, which is very stable, but dissolves in fuming nitric acid, D 1·52, yielding *dinitrodiphenyl*cyclo*butylmethane*, $C_3H_7\cdot CH(C_6H_4\cdot NO_2)_2$, m. p. 179°, whilst when boiled with nitric acid,

D 1·4, benzophenone and succinic acid are produced. When reduced with hydrogen iodide, diphenyl*cyclo*butylidenemethane forms a *hydrocarbon*, $C_{17}H_{18}$, m. p. 65°, isomeric with diphenyl*cyclo*butylmethane. Z. K.

Production of β-Benzopinacolin. NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1236—1237).—β-Benzopinacolin is most conveniently prepared by heating benzophenone with tin and fuming hydrochloric acid on the water-bath for about an hour, stirring the mixture from time to time. The mixture is then diluted with water, filtered, and the β-benzopinacolin is freed from tin by solution in boiling ethyl acetate, from which it crystallises in slender, colourless needles, m. p. 182·5°. Z. K.

A Method of Isolating Cholesterol and Cerebrosides from Brain by means of Saponification with Barium Hydroxide in Methyl Alcohol. J. LORRAIN SMITH and W. MAIR (*J. Path. Bact.*, 1910, **15**, 122).—Brain is hardened in formaldehyde, cut into slices, and dried. It is then pounded in a mortar, and extracted with chloroform in a Soxhlet apparatus. The chloroform is evaporated off, and the dry extract dissolved in methyl alcohol. A hot saturated solution of barium hydroxide in methyl alcohol is added, and the whole boiled with a reflux condenser for three hours. After cooling, the reaction should be alkaline. It is made nearly neutral by acetic acid, and evaporated to dryness. The residue is placed in a Soxhlet thimble, which is suspended in a wide-necked flask under a reflux condenser, and over acetone kept boiling on a water-bath. As cerebrosides are comparatively insoluble even in boiling acetone, a white precipitate soon appears. After six hours, the acetone contains practically all the cholesterol and most of the cerebrosides. The extraction is repeated with a fresh supply of acetone. The cerebrosides settle out on cooling the acetone; the cholesterol remains in solution. Lecithin and ordinary fats are by this method converted into insoluble barium soaps. W. D. H.

The Effect of Glycerol on the Clearing Point of Cholesterol and Cerebrosides. J. LORRAIN SMITH and W. MAIR (*J. Path. Bact.*, 1910, **15**, 122—123).—The clearing point of cholesterol (examined on the hot stage of a polarising microscope) is raised 5° by the presence of glycerol; that of cholesterol acetate is unaffected; the glycerol-cholesterol compound, if one exists, is easily decomposed by water, for, after the addition of water, cholesterol crystallises out unchanged.

On heating the white powder obtained by acetone from brain tissue, this substance (a cerebroside) assumes at 80° a fluid crystalline condition, and somewhat over 200° it clears sharply, showing only slight signs of decomposition; this corresponds with the melting point of other observers. When tested in glycerol, "myelin figures" appear at 100° and clear at 160°. When heated in water at comparatively low temperatures, the cerebroside gives myelin figures which are doubly refracting. W. D. H.

Phytosterol and Cholesterol. Ernst Salkowski (*Zeitsch. physiol. Chem.*, 1910, **69**, 473—475).—A discussion of the views of the author and of others on the relationships of cholesterol and the phytosterols. W. D. H.

Compounds of Aluminium Chloride and Bromide with Acid Chlorides. Boris N. Menschutkin (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 1310—1318. Compare Perrier, Abstr., 1903, i, 578).—Aluminium chloride forms a crystalline compound with benzoyl chloride, $AlCl_3$,BzCl, m. p. 93°. The concentration-temperature curve consists of three branches, with a eutectic point at −7·5° at the composition $AlCl_3$,6·53BzCl. When the mixture contains 61% aluminium chloride, viscid, resinous, vaselin-like substances are formed, which crystallise with great difficulty. Aluminium bromide yields a similar crystalline, molecular compound, $AlBr_3$,BzCl, m. p. 90°. The curve has two eutectic points, at −5° and composition $AlBr_3$,6·66BzCl, and at 7—8° at about the composition $AlBr_3$,0·54BzCl.

Aluminium halides behave towards organic acids as they do to alcohols and water, yielding halogen acid with development of much heat. Z. K.

Esters of *p*-Aminobenzoic Acid. Alfred Einhorn and Rudolf Seuffert (*Ber.*, 1910, **43**, 2995—3001).—The physiological value of diethylaminoethyl *p*-aminobenzoate has made it desirable to study other basic esters of *p*-aminobenzoic acid.

On heating chloroacetamide with ethyl *p*-aminobenzoate in presence of potassium iodide and sodium acetate, *ethyl* 2:5-*diketopiperazine*-1:4-*dibenzoate*, $CO_2Et\cdot C_6H_4\cdot N<\begin{matrix}CH_2\cdot CO\\CO\cdot CH_2\end{matrix}>N\cdot C_6H_4\cdot CO_2Et$, crystallising in rhombic prisms, m. p. 217—218°, is formed. From the mother liquors, the *glycinamide* of *ethyl* p-*aminobenzoate*, $CO_2Et\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO\cdot NH_2$, is obtained in long, thin needles, m. p. 142°.

When boiled with formaldehyde and diethylamine in alcoholic solution, *ethyl* p-*carboxyphenylglycinediethylaminomethylamide*,

$$CO_2Et\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot NEt_2,$$

is formed, crystallising in indefinite prisms, m. p. 97—98°.

With formaldehyde and piperidine, *ethyl* p-*carboxyphenylglycine-piperidinomethylamide*, $CO_2Et\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot C_5NH_{10}$, results; it crystallises in colourless needles, m. p. 102°. The *hydrochloride* crystallises in needles, m. p. 154°; the *hydrobromide* forms prisms, m. p. 162°.

On boiling an alcoholic solution of sodium *p*-nitrobenzoate, chloroacetamide and sodium iodide, p-*nitrobenzoyloxyacetamide*,

$$NO_2\cdot C_6H_4\cdot CO\cdot O\cdot CH_2\cdot CO\cdot NH_2,$$

is formed in needles, m. p. 171—172°. When heated with formaldehyde and diethylamine, ethyl *p*-nitrobenzoate is obtained. On reduction, *p*-aminobenzoyloxyacetamide results in the form of needles, m. p. 159—160°.

Ethyl p-*nitrobenzoyloxyacetate*, $NO_2\cdot C_6H_4\cdot CO\cdot O\cdot CH_2\cdot CO_2Et$, prepared by the interaction of sodium nitrobenzoate and ethyl chloroacetate, forms colourless needles, m. p. 39—40°. *Ethyl* p-*aminobenzoyl-*

oxyacetate crystallises in prismatic needles, m. p. 84°. p-*Carboxy-p-phenylglycinamide*, $CO_2H\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO\cdot NH_2$, prepared from sodium *p*-aminobenzoate, chloroacetamide and sodium iodide, forms prisms, m. p. 251°. E. F. A.

Some Derivatives of *p*-Aminobenzonitrile. Marston T. Bogert and Louis Elsberg Wise (*J. Amer. Chem. Soc.*, 1910, 32, 11, 1494—1499. Compare Bogert and Kohnstamm, Abstr., 1903, i, 559). —Improved methods are given for the preparation of *p*-nitro- and *p*-amino-benzonitriles, and some of their derivatives are described.

p-*Formylaminobenzonitrile* forms small, colourless crystals, m. p. 188—189° (corr.). A new method for the preparation of *p*-acetylaminobenzonitrile is given, which yields colourless needles, m. p. 205·5° (corr.). p-*Acetylaminobenzamide* crystallises in colourless prisms, m. p. 274·5°, with preliminary softening and sublimation. By the nitration of *p*-acetylaminobenzonitrile, 3-*nitro*-4-*acetylaminobenzonitrile* is obtained in long, yellow needles, m. p. 131·5° (corr.). p-*Benzoylaminobenzonitrile* melts at 170—170·5° (corr.); p-*benzenesulphonylaminobenzonitrile* forms colourless, arborescent crystals, m. p. 175—176° (corr.).

Methyl-p-*cyano-oxanilate*, $CO_2Me\cdot CO\cdot NH\cdot C_6H_4\cdot CN$, crystallises in leaflets, m. p. 208·5—209·5° (corr.); the *ethyl* derivative forms flat prisms, m. p. 188·5—189° (corr.). *Di*-p-*cyano-oxanilide*,

$$CN\cdot C_6H_4\cdot NH\cdot CO\cdot CO\cdot NH\cdot C_6H_4\cdot CN,$$

melts above 288°.

3 : 4-*Diaminobenzonitrile* crystallises in colourless needles, m. p. 147·5° (corr.). N. C.

Hydrogen Persulphide. V. Aldehydes and Hydrogen Persulphide. Ignaz Bloch, Fritz Höhn, and Günther Bugge (*J. pr. Chem.*, 1910, [ii], 82, 473—485. Compare Abstr., 1908, ii, 579).—When benzaldehyde and crude hydrogen persulphide interact in the presence of zinc chloride or hydrogen chloride, the mixture becomes warm and a brown resin is gradually deposited, which becomes solid on pouring into water. On shaking this resin with alcoholic potassium hydroxide, phenylcarbithionic acid (dithiobenzoic acid), $C_6H_5\cdot CS_2H$ (compare Abstr., 1906, i, 847), is formed, and can be readily isolated (see succeeding abstract). A similar reaction takes place with other aldehydes, salicylaldehyde giving *o-hydroxyphenylcarbithionic acid* (*dithiosalicylic acid*), $HO\cdot C_6H_4\cdot CS_2H$, and anisaldehyde yielding p-*methoxyphenylcarbithionic acid* (*dithioanisic acid*), $OMe\cdot C_6H_4\cdot CS_2H$. The two latter acids are crystalline and intensely coloured, whereas phenylcarbithionic acid is a violet oil. They are all unstable in the air, undergoing rapid oxidation with the formation of resins. The salts of the heavy metals are coloured and comparatively easily soluble in organic solvents, some of them being soluble in ether.

On gentle oxidation, the dithio-acids give rise to thioacyldisulphides. Methyl and ethyl esters can also be obtained.

In the preparation of these carbithionic acids it is immaterial whether crude hydrogen persulphide or pure hydrogen disulphide or trisulphide is used.

In the absence of a condensing agent the reaction proceeds differently.

If benzaldehyde is gradually added to cooled hydrogen disulphide, the liquid becomes brown, and after a time a white precipitate of an additive compound of 2 molecules of benzaldehyde with 1 molecule of hydrogen disulphide is formed. A similar compound results when hydrogen disulphide is replaced by hydrogen trisulphide. Anisaldehyde, cinnamaldehyde, and salicylaldehyde react similarly (compare Abstr., 1908, i, 900).

These compounds are white, well crystallised, and possess a more or less irritating odour. They are comparatively unstable, but the benzaldehyde compound with hydrogen disulphide may be preserved for months. The disulphide are more stable than the trisulphide compounds. On treatment with ice-cold hydrochloric acid they are split up into their components; alcoholic potassium hydroxide gives potassium polysulphides and the reaction products of the aldehyde with alkali. On recrystallising the trisulphide compounds from carbon disulphide, there is a tendency for sulphur to be lost, with the formation of the disulphide compounds.

From the analogy of hydrogen persulphide to hydrogen peroxide, the above additive compounds are considered to be *dibenzylidene disulphide hydroxide* and *dibenzylidene trisulphide hydroxide*, with the formulæ: OH·CHPh·S·S·CHPh·OH and

OH·CHPh·S·S·S·CHPh·OH

respectively (compare dibenzylidene peroxide hydroxide,

OH·CHPh·O·O·CHPh·OH).

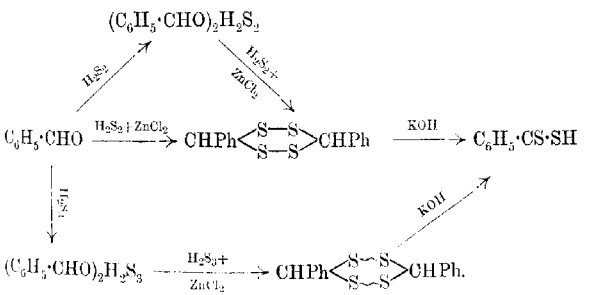
It is possible that the resinous intermediate product formed by the interaction of aldehydes and hydrogen persulphide in the presence of condensing agents is *dibenzylidene tetrasulphide*,

$$CHPh\begin{<}S{\cdot}S\\S{\cdot}S\end{>}CHPh,$$

corresponding with dibenzylidene peroxide, $CHPh\begin{<}O{\cdot}O\\O{\cdot}O\end{>}CHPh$.

This is supported by the fact that the analytical results agree approximately with the formula $C_{14}H_{12}S_4$; also, when dibenzylidene disulphide hydroxide is heated with zinc chloride or shaken with zinc chloride and hydrogen persulphide in the cold, the resinous intermediate product is formed, from which phenylcarbithionic acid is readily obtained.

The results obtained can be represented as follows:



Cinnamaldehyde behaves somewhat differently from the other aldehydes towards hydrogen persulphide. The methyl ester obtained from the resinous intermediate product contains two S-atoms in excess of that required by dithiocinnamic acid, and reacts with bromine without evolution of hydrogen bromide. The formula assigned to this ester is CSPh·CS·CS·SMe. Styrene also adds on sulphur, but the resulting compound will not further unite with bromine; thus hydrogen persulphide can be used to add on sulphur to unsaturated linkings. It behaves as a strong vulcanising agent towards rubber. T. S. P.

Dithio-acids (Carbithionic Acids). FRITZ HÖHN and IGNAZ BLOCH (*J. pr. Chem.*, 1910, [ii], 82, 486—511).—To a solution of crude hydrogen persulphide in benzene are added zinc chloride and benzaldehyde, shaking and cooling meanwhile. After twelve hours, the reaction mixture is heated on the water-bath, and finally treated with steam for three hours, after which time an orange-brown resin is formed, which, on pouring in water, solidifies to a vitreous, amorphous mass. A purer product is obtained by using pure hydrogen disulphide and hydrogen chloride as the condensing agent. It could not be obtained crystalline, although it is readily soluble in carbon disulphide; it has m. p. 80—90°, and decomposes at 120°. The analytical figures agree approximately with the formula $C_{14}H_{12}S_4$. To prepare phenylcarbithionic acid from this substance, it is shaken for two hours with a saturated alcoholic solution of potassium hydroxide, and the resulting brownish-red solution, after filtering from insoluble matter, treated in one of the two following ways: (1) carbon dioxide is passed into the solution, and, after collecting the precipitated potassium hydrogen and potassium ethyl carbonates, the greater part of the alcohol is expelled from the filtrate, which is then diluted with water. Lead acetate is carefully added to the solution until the lead sulphide precipitate first formed is succeeded by a red precipitate of lead phenylcarbithionate. The lead sulphide is then collected, and excess of lead acetate added to the filtrate to precipitate all the phenylcarbithionic acid. (2). The greater part of the alcohol is expelled from the solution, and the hydrogen persulphide destroyed with sulphurous acid. The phenylcarbithionic acid is then precipitated as an oil with hydrochloric acid, dissolved in benzene, and the lead salt formed by shaking the benzene solution with a solution of lead acetate in excess of potassium hydroxide. The yield of lead salt is 70—75% of the theory.

Lead phenylcarbithionate, $Pb(CS_2Ph)_2$, forms red needles from xylene, m. p. 200°. It is not decomposed by water, hydrogen sulphide, or dilute acids, but reacts readily with alkali sulphides, giving lead sulphide and a solution of the alkali phenylcarbithionate. Solutions of *potassium* and *sodium phenylcarbithionate* are fairly stable, but on evaporation on the water-bath partial decomposition takes place with the formation of a resin. They give no precipitates with barium, strontium, calcium, and magnesium salts, but with salts of the heavy metals characteristic precipitates are produced. The *zinc* salt forms yellow needles from benzene, and the *mercury* salt brownish-yellow needles or plates from benzene. The *silver* salt forms an unstable chocolate powder.

Phenylcarbithionic acid, $Ph\cdot CS_2H$, is obtained as a heavy, violet-coloured oil by the addition of hydrochloric acid to a solution of the potassium salt (compare Abstr., 1906, i, 847). The *methyl* ester, $Ph\cdot CS_2Me$, is readily obtained by the action of methyl sulphate on an alkaline solution of the potassium salt. It is a red oil with a peculiar disagreeable, although somewhat aromatic, odour, b. p. 154—157°/20 mm., 275—280°/760 mm. (decomp.); it oxidises in the air. The *ethyl* ester, $Ph\cdot CS_2Et$, is similar in properties to the methyl ester, and is obtained from silver phenylcarbithionate and ethyl iodide, b. p. 158—162°/13 mm., 165—168°/19 mm.

Salicylaldehyde was condensed with hydrogen persulphide in a similar manner to that described for benzaldehyde, hydrogen chloride being used as the condensing agent. From the condensation product, *lead* o-*hydroxyphenylcarbithionate*, $Pb(S_2C\cdot C_6H_4\cdot OH)_2$, was obtained as orange-yellow needles. It is much less stable than lead phenylcarbithionate, and undergoes decomposition on recrystallisation (from benzene or xylene); it is decomposed on warming with water. It was necessary to estimate the sulphur by decomposing the compound in a current of chlorine, using Schaefer's apparatus (Abstr., 1906, ii, 394). A solution of the *potassium* salt is obtained by treating the lead salt with a solution of potassium sulphide. It gives characteristic precipitates with salts of the heavy metals; the *mercury* salt forms bright yellow, microscopic needles.

o-*Hydroxyphenylcarbithionic acid*, $OH\cdot C_6H_4\cdot CS_2H$, obtained from the solution of the potassium salt by the addition of hydrochloric acid, forms orange-yellow needles from light petroleum, m. p. 48—50°, and slowly oxidises in the air. On treating the solution of the potassium salt with methyl sulphate, a mixture of *methyl* o-*hydroxyphenylcarbithionate*, $OH\cdot C_6H_4\cdot CS_2Me$, and *methyl* o-*methoxyphenylcarbithionate*,

$$OMe\cdot C_6H_4\cdot CS_2Me,$$

is obtained. The former forms yellow needles, m. p. 10—20°, and the latter orange-yellow lamellæ, m. p. 43—44°. *Ethyl* o-*hydroxyphenylcarbithionate*, $OH\cdot C_6H_4CS_2Et$, obtained from the silver salt and ethyl iodide, is an orange-yellow oil.

Oxidation of o-hydroxyphenylcarbithionic acid by leading air through the solution gives o-*hydroxythiobenzoyl disulphide*,

$$(OH\cdot C_6H_4\cdot CS)_2S_2;$$

brown leaflets from chloroform, m. p. 125—126°, to a blood-red liquid. A better yield (60%) is obtained by adding finely powdered sulphur to a methyl-alcoholic solution of the acid, hydrogen sulphide being evolved. Oxidation of the sodium salt of the acid with iodine or potassium ferricyanide is not a satisfactory method for preparing the disulphide. The *acetyl* derivative of the disulphide is obtained by acetylation with acetyl chloride in pyridine-glacial acetic acid solution; rose-colored powder, sinters at 74°, but only melts completely above 200°.

Lead p-*methoxyphenylcarbithionate*, $(OMe\cdot C_6H_4\cdot CS_2)_2Pb$, is obtained from the condensation product of anisaldehyde with hydrogen persulphide as a dark reddish-brown powder. It can be recrystallised without decomposition, and forms orange-yellow needles from benzene. The reaction with potassium sulphide is a reversible one. To prepare

the *potassium* salt, the free acid, obtained directly from the resinous condensation product by treatment with alcoholic potassium hydroxide and precipitation with hydrochloric acid, is dissolved in potassium hydroxide; it forms pale brownish-red needles. p-*Methoxyphenyl-carbithionic acid*, $OMe{\cdot}C_6H_4{\cdot}CS_2H$, can be obtained as pale brownish red crystals from light petroleum, but it is so unstable that it could not be prepared pure. A solution of the sodium or potassium salt gives characteristic precipitates with salts of the heavy metals; the *bismuth*, *zinc*, and *mercury* salts are crystalline. By oxidation of the potassium salt with iodine, a precipitate of p-*methoxythiobenzoyl disulphide*,

$$(OMe{\cdot}C_6H_4{\cdot}CS)_2S_2,$$

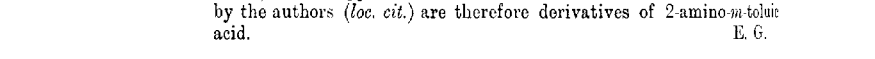
is obtained; m. p. 161—163°. *Methyl* p-*methoxyphenylcarbithionate* forms salmon-pink leaflets from methyl alcohol; m. p. 31° to a blood-red liquid. The *ethyl* ester forms yellow-orange needles, m. p. 25—26° to a red liquid.

A pure lead salt could not be obtained from the condensation product of cinnamaldehyde with hydrogen persulphide. By treating the condensation product directly with methyl sulphate, a substance was obtained possessing the formula $C_{10}H_8S_4$; orange-brown needles from methyl alcohol, m. p. 98—99° to a red liquid. The substance may probably be $CPhS{\cdot}CS{\cdot}CS_2Me$.

Pure hydrogen di- or tri-sulphide reacts with styrene, forming an almost colourless oil, with a very unpleasant odour. Phenanthrene and stilbene do not react with the pure hydrogen persulphides, whereas the latter are decomposed by linalool and geraniol. T. S. P.

Aminomethylbenzoic Acids [Aminotoluic Acids]. Henry L. Wheeler and Charles Hoffman (*Amer. Chem. J.*, 1910, 44, 507—508).—The acid obtained as the chief product of the nitration of *m*-toluic acid is not 4-nitro-*m*-toluic acid, as stated in an earlier paper (Abstr., 1910, i, 666), but is the 2-nitro-derivative, as was originally recorded by Jacobsen (Abstr., 1882, 185), and confirmed later by Findeklee (Abstr., 1906, i, 21) and Müller (Abstr., 1909, i, 160). The supposed derivatives of 4-amino-*m*-toluic acid described by the authors (*loc. cit.*) are therefore derivatives of 2-amino-*m*-toluic acid. E. G.

Ethyl Diazoacetate and *p*-Xylene. Eduard Buchner and Paul Schulze (*Annalen*, 1910, **377**, 259—284).—Ethyl diazoacetate reacts with *p*-xylene in much the same manner as with toluene (Buchner and Feldmann, Abstr., 1904, i, 57) and *m*-xylene (Buchner and Delbrück, *ibid.*, 1908, i, 87). Among the products is an ethyl dimethylnorcaradienenecarboxylate, which must be represented by one of the two formulæ:



The former of these is the more probable, as the ester is transformed readily into ethyl *β-p*-tolylpropionate, and, as in other cases, the $>CH{\cdot}CO_2Et$ group condenses with the carbon atoms of the hexa-ring which are as far removed from the methyl substituents as possible. The condensation product is therefore *ethyl* 2 : 5-*dimethyl*-$\Delta^{2:4}$-*norcara-*

dienenecarboxylate. On distillation, a 53—55% yield of an oil, b. p. 128—136°/12 mm., is obtained, but this contains, in addition to the above ester, two isomeridic condensation products, namely, appreciable amounts of an ethyl *cyclo*heptatrienecarboxylate and small amounts of ethyl *β-p*-tolylpropionate. The separation of these compounds is best accomplished by means of ammonia, as in the three esters the carbethoxy-group is attached repectively to secondary, tertiary, and primary carbon atoms (compare E. Fischer and Dilthey, Abstr., 1902, i, 269). It is an advantage to use a mixture of the methyl esters, as they react more readily with the ammonia. The addition of copper powder as a catalyst in the condensation does not give any better yields, but leads to the formation of appreciable amounts of methyl fumarate, a compound which is not formed in the absence of the metal.

2 : 5-*Dimethyl*-$\Delta^{2:4}$-*norcaradiene*-7-*carboxylamide*, $C_{10}H_{13}ON$, obtained by shaking the mixture of methyl esters for two days with a solution of ammonia saturated at 0°, crystallises from ethyl alcohol in colourless needles, m. p. 163—164°. The yield is small, only about 0·4 gram from 10 grams of condensation product. *β-p*-Tolylpropionamide is also formed, but is much more readily soluble in concentrated ammonia solution. The unsaturated amide turns yellow on exposure to the air, reduces permanganate, and dissolves in concentrated sulphuric acid to a red solution. When boiled with dilute sulphuric acid, it yields *p*-xylylacetic acid (compare Guerbet, Abstr., 1898, i, 424), and when heated for five minutes with 5% sodium hydroxide solution, yields an acid, m. p. 98—99°, which is probably 2 : 5-*dimethyl*-$\Delta^{2:4:7}$-*cycloheptatriene*-7-*carboxylic acid.*

The isomeric 2 : 5-*dimethyl*-$\Delta^{2:5}$-*cycloheptatriene*-7-*carboxylic acid*,

$$\begin{matrix} CH_2\cdot CMe{:}CH \\ | \\ CH{:}CMe{-}CH \end{matrix}\!\!>\!C\cdot CO_2H,$$

is most readily obtained by heating the crude condensation product for ten hours at 160—170° in an evacuated sealed tube, then distilling under reduced pressure, and hydrolysing with 25% methyl-alcoholic potassium hydroxide, first at the ordinary temperature and then for thirty minutes on the water-bath. On the addition of sufficient sulphuric acid to precipitate 40% of the total acid present, the pure crystalline acid is obtained, and the addition of more sulphuric acid precipitates 10—12 grams of crystalline *β-p*-tolylpropionic acid (Kröber, Abstr., 1890, 969). The $\Delta^{2:5:7}$-acid is formed together with the tolylpropionic acid when the crude condensation product is heated with 15% sulphuric acid for fifteen to thirty hours, and may also be obtained by heating the amide of the dicyclic acid for five hours with water in an evacuated tube at 160—170°, and subsequent hydrolysis. When a temperature of 180—190° is used, the ammonium salt of the heptatriene acid is formed directly. The $\Delta^{2:5:7}$-acid, $C_{10}H_{12}O_2$, crystallises from 30% ethyl alcohol or 30% acetic acid in long, pale yellow, glistening needles, m. p. 136—137°. Its solution in concentrated sulphuric acid is yellow, but gradually turns reddish-brown. The calcium, copper, lead, iron, zinc, and silver salts are all very sparingly soluble. The *methyl* ester has b. p. 120—121°/12 mm.; the *amide*,

$C_{10}H_{13}ON$, crystallises from water in colourless needles, m. p. 136—137°; the *dibromide*, $C_{10}H_{12}O_2Br_2$, crystallises from light petroleum in colourless needles, m. p. 126° (decomp.), after changing colour at 110°, and the *tetrabromide*, $C_{10}H_{12}O_2Br_4$, has m. p. 185° (decomp.), after turning yellow at 160°.

2 : 5-*Dimethyl*-$\Delta^{2:5}$-cyclo*heptadiene*-7-*carboxylic acid*, $C_7H_7Me_2\cdot CO_2H$, prepared by reducing the heptatriene acid with 3% sodium amalgam in alkaline solution whilst carbon dioxide is passed through, has m. p. 38—40° in the crude state, and is too unstable to purify. The *amide*, $C_{10}H_{15}ON$, prepared from the chloride, crystallises from water in needles, m. p. 142°, and turns yellow on exposure to the air. The *dihydrobromide*, $C_{10}H_{16}O_2Br_2$, obtained by leaving the acid in contact with glacial acetic acid saturated with hydrogen bromide at 0°, crystallises from light petroleum in small needles, m. p. 120° (decomp.), and when boiled for three hours with sodium hydroxide solution yields 2 : 5-*dimethyl*-$\Delta^{2:6}$-cyclo*heptadiene*-7-*carboxylic acid*,

$$\begin{matrix}CH_2\cdot CHMe\cdot CH\\ |\\ CH\cdot CMe—CH_2\end{matrix}\!\!>\!C\cdot CO_2H,$$

which crystallises from dilute alcohol in colourless needles, m. p. 82°. The corresponding *amide* has m. p. 147—148°, and turns yellow on exposure to the air. 2 : 5-*Dimethyl*cyclo*heptane*-7-*carboxylic acid*, $C_7H_{11}Me_2\cdot CO_2H$, is formed when an ethereal solution of the $\Delta^{2:5:7}$-triene acid is reduced with hydrogen in the presence of finely divided platinum ; it is an oil which does not solidify when kept in a freezing mixture, and yields an *amide*, $C_{10}H_{19}ON$, which crystallises from 30% alcohol in glistening needles, m. p. 185—186°. 7-*Bromo*-2 : 5-*dimethyl*cyclo*heptane*-7-*carboxylic acid*, $C_7H_{10}Me_2Br\cdot CO_2H$, prepared by the Volhard-Zelinsky method, crystallises from concentrated formic acid in stout, colourless needles, m. p. 152—153°, after softening at 120°.

β-p-*Tolylpropionamide*, $C_6H_4Me\cdot CH_2\cdot CH_2\cdot CO\cdot NH_2$, crystallises from hot water or ether in flat needles, m. p. 135°. The corresponding acid does not readily decolorise permanganate, and is oxidised by alkaline permanganate to terephthalic acid.

The conversion of the bicyclic condensation product into *p*-xylylacetic acid is represented as taking place by the addition and subsequent elimination of water, the intermediate hypothetical product being $\begin{matrix}CH\cdot CMe\cdot CH\cdot OH\\ |\\ CH\cdot CMe\cdot CH\cdot CH_2\cdot CO_2H\end{matrix}$. Similarly, with the conversion of the condensation product into β-*p*-tolylpropionic acid, a hypothetical intermediate product, formed by the addition of water, is assumed, namely, $CH(OH)_2\cdot CMe\cdot CH\cdot CH\cdot CMe\cdot CH_2\cdot CH_2\cdot CO_2H$.

The constitution of the 2 : 5-dimethyl-$\Delta^{2:5:7}$-cyclo*heptatriene*-7-carboxylic acid is discussed in detail. J. J. S.

Preparation of Substituted Cinnamic Acids. Theodor Posner (*J. pr. Chem.*, 1910, [ii], 82, 425—440).—The paper contains a description of the preparation of a large number of substituted cinnamic acids and their esters. The esters of nuclear-substituted

cinnamic acids are obtained best by boiling the acids for six hours with methyl or ethyl alcohol containing 10% of concentrated sulphuric acid. The following new compounds are described: m-*aminocinnamic acid acetate*, $C_9H_9O_2N,C_2H_4O_2$, is precipitated when acetic acid is added to the ammoniacal filtrate obtained after the reduction of *m*-nitrocinnamic acid by ferrous sulphate and ammonium hydroxide; it forms yellow crystals, m. p. 267° (decomp.). o-*Acetylaminocinnamic acid*, $NHAc{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO_2H$, m. p. 250—251°, is prepared from the acid and acetic anhydride. *Ethyl* o-*hydroxycinnamate*, m. p. 85—86°, is prepared by boiling *o*-coumaric acid with 2% alcoholic hydrogen chloride for six hours. *Methyl* p-*hydroxycinnamate* has m. p. 139—140°. *o*-Methoxycinnamic acid and its methyl ester are more conveniently obtained by methyl sulphate in the cold than by Perkin's method with methyl iodide at 150° (Trans., 1877, 39. 418). *β-o*-Methoxycinnamic acid is most conveniently obtained by boiling salicylaldehyde methyl ether (prepared from salicylaldehyde, aqueous sodium hydroxide, and methyl sulphate), sodium acetate, and acetic anhydride for nine hours. *m*-Methoxycinnamic acid is best prepared, although in only moderate yield, from *m*-methoxybenzaldehyde and malonic acid by Knoevenagel's method; its *methyl* ester has b. p. 305—307°/748 mm. The esterification of 3 : 4-dihydroxycinnamic acid by methyl alcohol and sulphuric acid yields anomalous results, the products being a *substance*, $C_{11}H_{12}O_4$, m. p. 131—132°, which is insoluble in sodium carbonate, and another *substance*, $C_{10}H_{10}O_4$, m. p. 159—160°, which is soluble in sodium carbonate and is reprecipitated by sulphuric acid. *Methyl* 3 : 4-*methylenedioxycinnamate* has m. p. 133—134°. *Ethyl β-phenyl-α-methylacrylate*, $CHPh{:}CMe{\cdot}CO_2Et$, conveniently prepared from ethyl propionate, sodium, and benzaldehyde in the cold, has b. p. 220—230°. *Methyl β-phenyl-α-ethylacrylate*, $CHPh{:}CEt{\cdot}CO_2Et$ b. p. 250—260°, is obtained in a similar manner from ethyl butyrate. *Methyl ββ-diphenylacrylate* has b. p. 194·6—194·8°/13 mm. C. S.

Crystallisation of Sodium Salicylate Solution. CHARLES A. HILL (*Pharm. J.*, 1910, [iv], **31**, 730—731).—Solutions of sodium salicylate, made by dissolving the commercial salt in its own weight of water, sometimes deposit spontaneously at the ordinary temperature in winter large masses of transparent crystals. This crystallisation is rarely obtained even below 0° unless the cold solution is inoculated with a crystal. The author obtained these crystals as large, well-defined prisms, exhibiting fluorescence and passing under the influence of heat or pressure into the anhydrous salt; analysis shows them to have the composition $C_7H_5O_3Na,6H_2O$.

The author also shows that commercial sodium salicylate is anhydrous. N. C.

Acylated Salicylic Acid Anhydrides. ALFRED EINHORN and RUDOLF SEUFFERT (*Ber.*, 1910, **43**, 2988—2995).—Acylated salicylic acids [*o*-acyloxybenzoic acids] are converted by the action of chlorocarboxylic acid alkyl esters in presence of pyridine into alkyl *o*-acyloxybenzoyl carbonates, and these, when warmed on the water-bath, form anhydrides. Other acid chlorides act similarly towards

o-acyloxybenzoic acids, yielding mixed anhydrides; these are decomposed on heating with the formation of the two simple anhydrides. The mixed anhydrides also slowly decompose at the ordinary temperature in contact with pyridine.

Ethyl o-acetoxybenzoyl carbonate, $OAc\cdot C_6H_4\cdot CO\cdot O\cdot CO\cdot OEt$, was obtained as a colourless, viscid oil. *Amyl o-acetoxybenzoyl carbonate* is a faintly yellow, viscid oil. The *valeryloxy-* and *benzoyloxy-ethyl* esters are likewise viscid oils. *Ethyl o-cinnamoyloxybenzoyl carbonate* crystallises in needles, m. p. 57°.

o-Acetyloxybenzoic anhydride, $(OAc\cdot C_6H_4\cdot CO)_2O$, crystallises in lustrous plates, m. p. 85°.

o-Benzoyloxybenzoic anhydride, $(OBz\cdot C_6H_4\cdot CO)_2O$, forms prismatic needles, m. p. 110—111°. *o-Cinnamoyloxybenzoic anhydride*, $(CHPh:CH\cdot CO\cdot O\cdot C_6H_4\cdot CO)_2O$, separates in refractive prisms, m. p. 129—130°.

Benzoic o-acetyloxybenzoic anhydride, $C_6H_4(OAc)\cdot CO\cdot O\cdot CO\cdot C_6H_5$, crystallises in needles, m. p. 75—76°. *Benzoic o-benzoyloxybenzoic anhydride* crystallises in rhombic plates, m. p. 74—75°. *Cinnamic o-cinnamoyloxybenzoic anhydride* forms needles, m. p. 78—79°.

E. F. A.

Derivatives of Camphoroxalic Acid. XIII. J. Bishop Tingle and S. J. Bates (*J. Amer. Chem. Soc.*, 1910, **32**, 11, 1499—1517. Compare Abstr., 1899, i, 444; 1900, i, 302; 1901, i, 632; 1905, i, 799; 1906, i, 902; 1908, i, 125, 126).—The authors have made a further study of the condensation products of camphoroxalic acid and amines, and the action of various reagents on them. The results confirm the view that the constitution of these compounds is given by the formula $C_8H_{14}<\begin{matrix}C:CR\cdot NR^1R^2\\ |\\ CO\end{matrix}$, where R = H or CO_2H; R^1 and R^2 = H, alkyl or aryl.

A comparison between the compounds resulting from the condensation of camphoroxalic acid with thiosemicarbazide and with semicarbazide shows that in the former there is much less tendency to form cyclic derivatives.

Phenylcamphoformeneaminecarboxylic acid, $C_8H_{14}<\begin{matrix}C:C(NHPh)\cdot CO_2H\\ |\\ CO\end{matrix}$, was prepared by the method of Bishop Tingle and A. Tingle, and the effect of bromine, chlorides of phosphorus, and oxidising agents observed. By the action of methyl sulphate, *methyl phenylcamphoformeneaminecarboxylate* is obtained as yellow crystals, m. p. 127°. *Methyl methoxycamphoroxalate*, $C_8H_{14}<\begin{matrix}C:C(OMe)\cdot CO_2Me\\ |\\ CO\end{matrix}$, is obtained as an oil by the action of methyl sulphate and sodium carbonate on methyl camphoroxalate.

Thiosemicarbazylcamphoformeneaminecarboxylic acid, $C_8H_{14}<\begin{matrix}C:C(CO_2H)\cdot NH\cdot NH\cdot CS\cdot NH_2\\ |\\ CO\end{matrix}$, exists in two modifications, one melting at 148—149°, the other at

120—125°. By fusion it forms a *compound*, m. p. 170°. The *ethyl* ester of the acid forms white crystals, m. p. 150—151°. By the action of acetic anhydride on the acid, *thiosemicarbazylcamphoformeneaminecarboxylactimide*, $\begin{matrix}C_8H_{14}\\ |\\ CO\end{matrix}\!\!>\!C{:}C\!<\!\begin{matrix}CO\text{—}NH\\ |\\ NH{\cdot}NH\end{matrix}\!\!>\!CS$, is obtained as bright red crystals, m. p. 181—182°.

m-4-Xylidine m-4-xylidylcamphoformeneaminecarboxylate,

$$\begin{matrix}C_8H_{14}\\ |\\ CO\end{matrix}\!\!>\!C{:}C\!<\!\begin{matrix}CO_2{\cdot}NH_3{\cdot}C_6H_3Me_2\\ |\\ NH{\cdot}C_6H_3Me_2\end{matrix},$$

forms brown crystals, m. p. 93—94°; the *acid* crystallises in yellow crystals, m. p. 117—118°.

p-Chlorophenylcamphoformeneaminecarboxylic acid crystallises in yellow needles, m. p. 182—183°.

p-Chlorophenylcamphoformeneamine, $C_8H_{14}\!<\!\begin{matrix}C{:}CH{\cdot}NH{\cdot}C_6H_4Cl\\ |\\ CO\end{matrix}$, forms white crystals, m. p. 194—195°.

Dibenzylamine camphoroxalate has m. p. 135—136°.

Dibenzylamine phenylcamphoformeneaminecarboxylate,

$$C_8H_{14}\!<\!\begin{matrix}C{:}C(NHPh){\cdot}CO_2{\cdot}NH_2(CH_2Ph)_2\\ |\\ CO\end{matrix},$$

forms white crystals, m. p. 185°. *m-Carboxyphenylcamphoformeneaminecarboxylic acid* crystallises in white crystals, m. p. 136—137°. By the action of heat on the acid, *m-carboxyphenylcamphoformeneamine*, $C_8H_{14}\!<\!\begin{matrix}C{:}CH{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H\\ |\\ CO\end{matrix}$, is obtained in long, yellow needles, m. p. 116—117°.

By the condensation of benzidine and camphoroxalic acid, a yellow substance, m. p. 208°, is produced, which is probably an inner ammonium salt, and has the constitution $\begin{matrix}C_8H_{14}\\ |\\ CO\text{—}\end{matrix}\!\!>\!C{:}C\!<\!\begin{matrix}CO{\cdot}O{\cdot}NH_3\\ |\\ NH\text{—}C_{12}H_8\end{matrix}$.

Benzidylcamphoformeneamine, $C_8H_{14}\!<\!\begin{matrix}C{:}CH{\cdot}NH{\cdot}C_{12}H_8{\cdot}NH_2\\ |\\ CO\end{matrix}$, melts at 317—318°. By the condensation of camphylamine and camphoroxalic acid, a small quantity of a white *sublimate*, m. p. 105°, is obtained. N. C.

Chemistry of Alcapton-urine (Homogentisic Acid and Certain of its Derivatives). Carl Th. Morner (*Zeitsch. physiol. Chem.*, 1910, 69, 329—365).—Homogentisic acid in the presence of ammonia and air gives, not only the brown coloration described by earlier authorities, but, under suitable conditions, an intensely brilliant reddish-violet coloration. The conditions necessary for the production of the coloration are: (*a*) concentration of homogentisic acid 0·25 to 2%. With more dilute solutions, yellowish-brown, and with more concentrated solutions blackish-brown, colorations are obtained. (*b*) Concentration of the ammonia 1 to 4%. (*c*) Oxygen concentration. It is essential that the amount of oxygen absorbed per unit of time shall not be too large. This is accomplished by using comparatively narrow tubes; thus with 20 c.c. of liquid, the reaction was given when tubes of 0·75 to 2·0 cm.

diameter were used, but only brown or brownish-red colorations were obtained with tubes 3·0 to 5·0 cm. diameter. If the volume of liquid is large and the tube very narrow, the time required for the coloration to appear may be considerable. Moderately concentrated solutions of many substances, for example, ammonium sulphate or chloride (1/50 saturated), potassium chloride (1/4—1/3 saturated), potassium hydroxide (1%), aniline (1/2%), carbamide (8%), alcohol (20%), prevent the formation of the coloration. Glycerol, dextrose, and sucrose at concentrations of 20% have no effect, and sodium chloride or sulphate solutions up to 1/3 saturated do not interfere. It has been found possible to isolate small amounts of two distinct compounds from the reddish-purple solution. These are termed α- and *β-alcaptochromes*. The α-compound crystallises from hot water in thin, hexagonal plates, with a metallic lustre and green reflex, and when heated above 105° decomposes without melting or subliming. It is only sparingly soluble in most solvents; the solutions have a yellow colour and do not fluoresce. The orange-yellow pyridine solution, when diluted with water, turns blood- or cherry-red. The compound is acidic, and dissolves in dilute alkali solutions, yielding colorations which resemble methyl-violet solutions. Such solutions are readily decolorised by the addition of a solution of ferrous sulphate plus a tartrate, but the colour is restored on shaking with air. The solutions in sodium or potassium hydrogen carbonate have a somewhat more reddish colour, and this changes to yellow when carbon dioxide is passed in.

The solution in ammonium hydroxide has a violet colour, and the colour can be detected with a dilution of 1 in 20 millions; it becomes more red when heated, but returns to the original colour as it cools. The *ammonium* salt has been isolated as a solid with a green, metallic lustre. The acid also dissolves in concentrated sulphuric or hydrochloric acids, but does not appear to yield salts with them. The constitution suggested for the α-alcaptochrome is that of a *4-imino-p-benzoquinone-2-acetic acid*, $NH{:}C_6H_3O{\cdot}CH_2{\cdot}CO_2H$.

The following hydroxylic derivatives do not yield colorations when treated in the same manner as homogentisic acid. Catechol, resorcinol, *β*-resorcylic acid, phloroglucinol, pyrogallol, gallic acid, tannin, protocatechuic acid. Neither do quinol, quinhydrone, dianilinoquinol, quinol dimethyl ether, arbutin, or gentisic acid. Toluquinol, on the other hand, gives an intense reddish-violet solution with an orange fluorescence. The coloured substance has been isolated as a magma of reddish-brown, crystalline needles, which dissolve in alkalis, yielding solutions with a reddish-violet colour and orange fluorescence. The addition of acetic acid or carbon dioxide to such solutions precipitates the colouring matter.

Hydroxyquinol gives a bluish-violet-coloured non-fluorescent solution. The coloured compound has been isolated as an amorphous, violet-brown, flocculent mass, insoluble in most solvents.

The coloration described by Langstein and Meyer (*Arch. Klin. Med.*, 1903, 78, 161) as characteristic of homogentisic acid lactone is quite different from the alcaptochrome reaction, and by means of the latter it is shown that ammonium hydroxide solutions do

not readily hydrolyse the lactone, whereas solutions of sodium hydroxide do.

It is shown that many aromatic derivatives containing free hydroxyl groups in positions 1 and 4 react with aniline in the presence of air, yielding coloured, crystalline compounds, which are insoluble in water, but dissolve in organic solvents, and also give characteristic colorations with concentrated sulphuric acid. The method of procedure consists in mixing an aqueous solution of the hydroxy-compound with sufficient saturated aqueous solution of aniline or one of its homologues, and exposing to the air for several weeks in shallow dishes. The amorphous precipitates are removed, washed with 1% potassium carbonate solution, then with water, and crystallised from glacial acetic acid.

Quinol yields 2 : 5-dianilo-*p*-benzoquinone with aniline, 2 : 5-*p*-toluidino-*p*-benzoquinone with p-toluidine, and 2:5-*m*-xylidino-*p*-benzoquinone with *m*-xylidine.

Homogentisic acid (or alcapton-urine) and aniline under the given conditions yield 3 : 6-*dianilino-p-benzoquinone-3-acetic acid*,

$$CH\begin{<}CO\cdot C(NHPh)\\C(NHPh)\cdot CO\end{>}C\cdot CH_2\cdot CO_2H,$$

which crystallises from glacial acetic acid in brownish-violet prisms with a coppery lustre, m. p. 228°. With sulphuric acid it gives a magenta-red coloration, which changes rapidly to cherry-red. The corresponding p-*toluidino*-derivative, $C_{32}H_{26}O_4N_2$, forms dark reddish-brown crystals, m. p. 231°, and gives a pure blue coloration with concentrated sulphuric acid; the m-*xylidino*-derivative, $C_{34}H_{34}O_4N_2$, forms brownish-yellow crystals, m. p. 211°, and also gives a blue coloration with sulphuric acid.

Quinhydrone, homoquinol, hydroxyquinol, gentisic acid, and 3-methoxy-1-propyl-2 : 5-quinol also react with aniline and air in a similar manner.

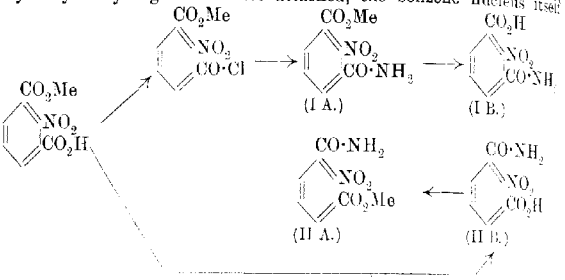
Homogentisic acid lactone acts very slowly with aniline and air, and then probably only as the result of hydrolysis; quinol dimethyl ether does not react.

The product described previously (Abstr., 1909, ii, 331) as obtained from normal urine, aniline, and air is also formed in the absence of urine if a small amount of a catalyst, for example, a ferrous salt, is present, and is regarded as dianilino-*p*-benzoquinonemonoanil. Its formation in the case of urine is due to the presence of small amounts of some catalyst, and not to the presence of quinol.

J. J. S.

Ester-acids and Amido-acids of the *iso*Phthalic Acid Series. The Question of Equivalence of Positions 2 and 6 in the Benzene Nucleus. ALFRED WOHL (*Ber.*, 1910, 43, 3474—3489).—The non-existence of two isomeric ortho-disubstituted derivatives of benzene is usually explained at the present time by the assumption that the free affinities of the six nuclear carbon atoms are not arranged in three separate pairs of unsaturated systems, but are so distributed that they mutually neutralise one another. The isomerism of 1 : 2- and 1 : 6-derivatives,

if such are capable of existence, is due, not to the movements of a migratory atom or group as in typical cases of tautomerism, but to a difference in the distribution of the free affinities of the carbon atoms. Hitherto, all attempts to discover isomeric ortho-disubstituted benzene derivatives have depended on reactions which seek to introduce substituents directly into positions 2 or 6, that is, on reactions which interfere with the benzene nucleus itself, the natural result being that the free affinities of the nuclear carbon atoms become arranged in the position of greatest stability, and only one ortho-disubstituted derivative has been discovered. The author's method of attacking the problem is indicated by the annexed scheme; only the hydroxylic hydrogen atoms are attacked, the benzene nucleus itself



being uninterfered with. The substances I A and II A are found to be identical, not isomeric, and so also I B and II B. Similar results have been obtained with 2-hydroxy*iso*phthalic acid and with *iso*phthalic acid itself.

[With E. NAGELSCHMIDT.]—*Methyl hydrogen* iso*phthalate*, $CO_2H\cdot C_6H_4\cdot CO_2Me$, m. p. 193°, is obtained by boiling a methyl-alcoholic solution of methyl *iso*phthalate and one equivalent of sodium hydroxide for two to three hours, filtering any precipitated sodium salt, pouring the filtrate into water, extracting the unchanged ester with ether, and carefully acidifying the aqueous solution with hydrochloric acid; the first portion of the precipitate is almost pure methyl hydrogen *iso*phthalate. This is converted by thionyl chloride into the *chloride*, $CO_2Me\cdot C_6H_4\cdot COCl$, which reacts with cold concentrated aqueous ammonia to form the *amide*-ester, $CO_2Me\cdot C_6H_4\cdot CO\cdot NH_2$, m. p. 148·5° (corresponding with I A above); by hydrolysis with methyl-alcoholic sodium hydroxide the amide-ester yields the *amic-acid*, $CO_2H\cdot C_6H_4\cdot CO\cdot NH_2$, m. p. 280° (I B). The amic-acid (II B), obtained by treating methyl hydrogen *iso*phthalate with methyl-alcoholic ammonia, has m. p. 280°, is identical with the preceding amic acid, and is converted into the amide-ester, m. p. 148·5° (II A, identical with I A), by shaking the potassium salt obtained from it by methyl-alcoholic potassium methoxide with methyl sulphate. *Ethyl hydrogen* iso*phthalate*, prepared like the corresponding methyl ester, has m. p. 115—117°.

Methyl 2-*nitro*iso*phthalate*, $NO_2\cdot C_6H_3(CO_2Me)_2$, m. p. 135°, obtained by

boiling the acid with methyl alcohol and concentrated sulphuric acid, is converted into the following compounds by reactions similar to the preceding. *Methyl hydrogen 2-nitroisophthalate*, $CO_2H\cdot C_6H_3(NO_2)\cdot CO_2Me$, m. p. 197°; *ester-chloride*, m. p. 121°; *ester-amide*, m. p. 190—191°; *amic-acid*, m. p. 252°.

Methyl hydrogen 2-hydroxy*iso*phthalate, by treatment with aqueous methyl-alcoholic ammonia, yields the *amic acid*,

$$CO_2H\cdot C_6H_3(OH)\cdot CO\cdot NH_2,$$

m. p. 245° (decomp.), which is converted into the *amide-ester*, $CO_2Me\cdot C_6H_3(OH)\cdot CO\cdot NH_2$, m. p. 185°, by treatment with potassium methoxide, and subsequently with methyl sulphate, as above. Attempts to prepare the ester-chloride, $CO_2Me\cdot C_6H_3(OH)\cdot COCl$, have not been very successful. Methyl hydrogen 2-hydroxy*iso*phthalate is dehydrated by thionyl chloride, yielding a *substance*, $C_9H_6O_4$, which is probably a multimolecular β-lactone,

$$\left(CO_2Me\cdot C_6H_3\!<\!\begin{matrix}O\\|\\CO\end{matrix}\right)_x,$$

is converted by acetyl chloride and phosphorus pentachloride into the acetylated anhydride described below, and reacts with phosphorus pentachloride alone to form an impure ester-chloride, from which, however, an ester-amide, m. p. 185°, identical with the above, can be prepared.

Methyl hydrogen 2-hydroxy*iso*phthalate is converted by acetic anhydride and one drop of concentrated sulphuric acid at 40—50° into the *acetoxy*-derivative, $CO_2Me\cdot C_6H_3(OAc)\cdot CO_2H$, m. p. 118—119°, but when heated with acetyl chloride on the water-bath, yields an acetylated *anhydride*, $C_{22}H_{18}O_{11}$, m. p. 144—146°, which does not give a colour reaction with ferric chloride, and is only slowly converted into the original ester-acid by hot water.

When boiled with methyl alcohol and sulphuric acid, 2-hydroxy*iso*phthalic acid yields the *methyl* ester, $OH\cdot C_6H_3(CO_2Me)_2$, m. p. 72°, the potassium salt of which, obtained by interaction with methyl-alcoholic potassium methoxide, reacts with the calculated quantity of methyl sulphate, diluted with twice its weight of benzene, to form a *substance*, $C_{11}H_{12}O_5$, b. p. 170—171° 11 mm., to which the constitution $CO_2Me\cdot C_6H_3\!<\!\begin{matrix}O\\|\\C(OMe)_2\end{matrix}$ is given. When the potassium salt is heated with methyl sulphate alone, it is converted into a *substance*, $C_{11}H_{12}O_8S$, m. p. 110°, which has acidic properties, develops a wine-red coloration with ferric chloride in aqueous acetone, and retains its sulphur after being boiled with hydrochloric acid; probably it is the trimethyl ester of 2-hydroxy-5-sulpho-*iso*phthalic acid. C. S.

Δ^1-Tetrahydrobenzaldehyde from *cyclo*Hexanone. Walther Borsche and R. Schmidt (*Ber.*, 1910, 3400—3401).—o-*Hydroxyhexahydrobenzylaniline*, $OH\cdot C_6H_{10}\cdot CH_2\cdot NHPh$, obtained by reducing the anil of hydroxymethylene*cyclo*hexanone (Abstr., 1910, i, 881) with sodium and boiling alcohol, crystallises from dilute alcohol in colourless plates, m. p. 98—100°, and on oxidation with chromic anhydride in glacial acetic acid solution yields aniline-black and Δ^1-tetrahydrobenzaldehyde (Wallach, Abstr., 1906, i, 565). The method is not a suitable one for

the preparation of the aldehyde, as the yield is only about 10% of the theoretical (compare Farbwerke vorm. Meister, Lucius & Brüning, Abstr., 1902, i, 102). J. J. S.

Anthranil. XVIII. Methods of Preparation of *o*-Nitrosobenzaldehyde. EUGEN BAMBERGER and ANDOR FODOR (*Ber.*, 1910, **43**, 3321—3335).—For one reason or another *o*-nitrosobenzaldehyde cannot be prepared by the oxidation of *o*-hydroxylaminobenzaldehyde, the electrolytic reduction of *o*-nitrobenzaldehyde, the reduction of *o*-nitrobenzyl chloride by zinc and acetic acid, or by the oxidation of *o*-hydroxylaminobenzaldoxime or of anthranilphenylhydrazine by ferric chloride. It can be prepared by the following methods, none of which, however, are really satisfactory: (1) Hydrochloric acid and sodium nitrite are allowed to react with anthranil under the conditions mentioned by Bamberger and Lublin (Abstr., 1909, i, 503), and the resulting white, crystalline crust on the sides and bottom of the vessel is separated mechanically from the yellow precipitate of *o*-aldehydophenylnitrosohydroxylamine, washed with water at 0°, and purified by distillation with steam. (2) It has been isolated from the products of the hydrolysis of *o*-aldehydophenylnitrosohydroxylamine by dilute sulphuric acid (*loc. cit.*). (3) An alkaline solution of *o*-aldehydophenylnitrosohydroxylamine is treated with not too large a quantity of 3% potassium permanganate at 0°; the ethereal extract of the resulting solution contains *o*-nitrosobenzaldehyde. It is also formed when the oxidation is performed in 2*N*-sulphuric acid at 0°. (4) The oxidation of anthranil in 2*N*-sulphuric acid at 0° by 3% potassium permanganate also yields *o*-nitrosobenzaldehyde; when too much of the oxidising agent is added, *o*-nitrobenzaldehyde is produced; *p-nitrophenylhydrazone*, m. p. 257·5—258·5° (decomp.). The production of *o*-nitrosobenzaldehyde by the oxidation of anthranil furnishes a final argument against Heller's contention, that anthranil and methylanthranil are not similarly constituted homologues, because the former yields *oo'*-azoxybenzoic acid, the latter *o*-nitrosoacetophenone, by oxidation (Abstr., 1908, i, 267; compare also Bamberger and Lublin, *loc. cit.*).

o-Nitrosobenzaldehyde has m. p. 113—113·5° with previous blackening, not 109—110° as stated previously. It can be purified by very rapid distillation with steam, although the loss by decomposition is great. Its solutions have a grass-green colour, which is generally intensified by warming. C. S.

Persulphides of Aldehydes. GÜNTHER BUGGE and IGNAZ BLOCH (*J. pr. Chem.*, 1910, [ii], **82**, 512—519. Compare this vol., i, 46).—To 18 grams of freshly distilled benzaldehyde are gradually added 4·5 c.c. of pure hydrogen disulphide. The liquid becomes warm, turns yellow in colour, and after a time gives a white precipitate of *dibenzylidene disulphide hydroxide*, OH·CHPh·S·S·CHPh·OH; silvery plates or prisms from carbon disulphide; very stable when pure, but decomposes on heating; the molecular weight, determined cryoscopically in bromoform solution, was 257. It is decomposed by alcoholic potassium hydroxide, potassium polysulphide, potassium benzoate, and benzyl alcohol being produced, but no phenylcarbithionic acid. On heating with zinc chloride, it gives a condensation product,

from which phenylcarbithionic acid is readily obtained. The same condensation product may also be obtained in the cold by treatment with hydrogen persulphide.

Dibenzylidene trisulphide dihydroxide, $OH\cdot CHPh\cdot S_3\cdot CHPh\cdot OH$, is similarly obtained from benzaldehyde and hydrogen trisulphide; white prisms from carbon disulphide; it is much less stable than the disulphide hydroxide, showing a great tendency to lose sulphur, but is similar to it in its reactions.

Dianisylidene disulphide dihydroxide, $[OMe\cdot C_6H_4\cdot CH(OH)]_2S_2$, and *dianisylidene trisulphide dihydroxide*, $[OMe\cdot C_6H_4\cdot CH(OH)]_2S_3$, are similar in properties to the dibenzylidene compounds. The trisulphide hydroxide is very unstable, sinters at 25°, m. p. 47—55° with decomposition.

The preparation of *dicinnamylidene disulphide dihydroxide*, $[CHPh:CH\cdot CH(OH)]_2S_2$, is not always successful; it forms white crystals, which sinter at 26° and decompose between 37° and 40°, and unites with bromine, as also does *dicinnamylidene trisulphide hydroxide*, $[CHPh:CH\cdot CH(OH)]_2S_3$; this forms white crystals, decomposing at 35°, which at times are very unstable.

The additive compounds of salicylaldehyde with the hydrogen persulphides could not be obtained pure, as they are only stable below −10°. T. S. P.

Hydropinenealdehyde and Hydropinenecarboxylic Acid. Josef Houben and Hans Doescher (*Ber.*, 1910, **43**, 3435—3442. Compare Abstr., 1908, i, 27).—A somewhat modified method for the preparation of hydropinenealdehyde is described; when carefully sublimed it is obtained as colourless needles, m. p. 131°. The oxime, when boiled with acetic anhydride for three hours, yields the *nitrile* of hydropinenecarboxylic acid, $\begin{matrix}CH_2\text{--}CH\\ |\\ CH_2\cdot CMe\end{matrix}\!\!>\!CMe_2\!<\!\!\begin{matrix}CH_2\\ |\\ CH\cdot CN\end{matrix}$, which crystallises from 60% alcohol in slender needles, m. p. 163°. The aldehyde gives Doebner's reaction with β-naphthylamine and pyruvic acid (Abstr., 1894, i, 261, 532), yielding the *β-naphthacinchonic acid*, $C_{10}H_{16}\!<\!\!\begin{matrix}N=\!\!=\!\!=C\cdot C_{10}H_7\\ |\\ C(CO_2H):CH\end{matrix}$, m. p. 294°.

The hydropinenecarboxylic acid, obtained by oxidising the aldehyde by exposure to the air, crystallises from 60% alcohol, and has m. p. 88—90°, after sintering at 80°. The acid prepared from magnesium pinene hydrochloride has m. p. 72—74° (Houben, Abstr., 1906, i, 21), and from bornyl iodide, 69—71° (Zelinsky, *ibid.*, 1903, i, 185). The *ethyl* ester, $C_{13}H_{22}O_2$, is a pleasant-smelling oil, with b. p. 116—117°/12·5 mm.; it can be obtained pure by the esterification of the acid or in an impure form by the action of ethyl chloroformate on magnesium pinene hydrochloride, and on hydrolysis yields an acid, m. p. 82°, the analytical data of which do not agree with those of a hydropinenecarboxylic acid. The *anhydride*, $(C_{10}H_{17}\cdot CO)_2O$, can be prepared by heating the acid with excess of acetyl chloride, removing the excess, and heating the residue at 200° under atmospheric pressure; it crystallises from alcohol in small needles, m. p. 210°, and when boiled

with 5% potassium hydroxide solution yields an acid, m. p. 78°. The *amide*, $C_{10}H_{17}\cdot CO\cdot NH_2$, is formed together with the ammonium salt of the acid by the action of dry ammonia on a chloroform solution of the anhydride. It crystallises from light petroleum in small prisms, m. p. 138—139°. The *anilide*, $C_{10}H_{17}\cdot CO\cdot NHPh$, crystallises in glistening, felted needles, m. p. 151°.

The acid obtained from the aldehyde appears to be a mixture.

J. J. S.

Action of Sodium Disulphide on 4-Nitro-2-methoxytoluene. Jan J. Blanksma (*Rec. trav. chim.*, 1910, **29**, 407—409).—4-Nitro-2-methoxytoluene was prepared by the method of Nölting and Collin (Abstr., 1884, ii, 1006). When it is treated with sodium sulphide and sulphur and distilled, the distillate yields colourless crystals of *2-methoxy-p-toluidine*, m. p. 58°; the *acetyl* derivative crystallises in colourless leaflets, m. p. 130°. The residue after distillation yields *4-amino-2-methoxybenzaldehyde* as colourless crystals, m. p. 136°; the *acetyl* derivative melts at 145°.

4-Hydroxy-2-methoxybenzaldehyde and 2 : 4-dimethoxybenzaldehyde were also prepared from 4-amino-2-methoxybenzaldehyde. N. C.

Some Derivatives of 3-Nitrocumaldehyde. G. Pizzuti (*Gazzetta*, 1910, **40**, ii, 236—241).—*3-Nitrocumaldehydeoxime*, $C_{10}H_{12}O_3N_2$, crystallises in colourless needles, m. p. 74—76°, which become reddish-yellow in the light. *3-Nitrocumaldehydephenylhydrazone*, $C_{16}H_{17}O_2N_3$, forms red scales, m. p. 123° (giving a yellow liquid), and also long, red needles, m. p. 120°. *3-Nitrocumaldehydesemicarbazone*, $C_{11}H_{14}O_3N_4$, crystallises in rosettes of colourless needles, m. p. 222° (previously softening); when exposed to light, the substance becomes yellow. 3-Nitrocumaldehyde condenses with rhodanic acid, yielding *3-nitro-4-isopropylbenzylidenerhodanic acid*, $C_{13}H_{12}O_3N_2S_2$ (compare Bargellini, Abstr., 1906, i, 536), which forms bright yellow scales, m. p. 180°. The compound dissolves in concentrated sulphuric acid, producing a pale yellow coloration. When 3-nitrocumaldehyde is warmed with 1 molecule of phenylmethylpyrazolone in alcoholic solution, a *compound*, $C_{19}H_{19}O_3N_3$, resulting from the combination of equimolecular quantities of the two substances, is obtained. It forms yellow scales, which begin to decompose at 180°, and at 205—208° are completely fused and decomposed, with production of a red liquid. When two molecules of the pyrazolone are taken in the reaction, a *compound* containing 10·66—10·69% of nitrogen is obtained. It crystallises in pale yellow needles, m. p. 151—153° (becoming red at 140°). When kept at 100°, it loses 4% in weight. The substance remaining contains the same percentage of nitrogen as the compound $C_{19}H_{19}O_3N_3$ mentioned above, but it still has m. p. 153°. R. V. S.

Trimethylene [*cyclo*Propane] Derivatives. Louis Michiels (*Bull. Soc. chim. Belg.*, 1910, **24**, 396—416).—A number of *cyclo*propane derivatives have been prepared, and their interaction with various reagents investigated, with a view to comparing the behaviour of the trimethylene residue with isomeric open-chain groups. The results

show that the trimethylene residue exhibits a specific character, and that in particular the hydrogen atom of the :CH group is less easily replaced than in the corresponding *iso*propyl derivatives. The *cyclo*propyl series of alcohols, whether primary or secondary, are readily esterified by haloid acids (compare Bruylants, Abstr., 1909, i, 226).

cyclo*Propyl propyl ketone*, $COPr^{\alpha}\cdot CH<\begin{matrix}CH_2\\CH_2\end{matrix}$, D^{20} 0·9077, n_D 1·43733, b. p. 150°/747 mm., is a colourless, mobile liquid with a mint-like odour. cyclo*Propyl butyl ketone*, D^{20} 0·8782, n_D 1·43513, b. p. 171—172°/747 mm., resembles its lower homologue in odour and appearance, as does also cyclo*propyl* iso*butyl ketone*, D^{20} 0·8735, n_D^{20} 1·43282, b. p. 161°/757 mm. These three ketones were prepared by Bruylants' method (*loc. cit.*), using the magnesium alkyl bromide appropriate to each case.

Attempts to prepare *di*cyclo*propyl ketone* by the catalytic action of heated alumina or thoria on *cyclo*propanecarboxylic acid or its ethyl ester were unsuccessful, although in one experiment a *product*, boiling at 160—170°, and yielding a *semicarbazone*, m. p. 85—86°, was obtained.

cyclo*Propyl chloromethyl ketone*, $C_3H_5\cdot CO\cdot CH_2Cl$, D^{20} 1·2036, n_D 1·46235, b. p. 180°/762 mm., or 103°/40—45 mm., obtained by the action of sulphuryl chloride on *cyclo*propyl methyl ketone, is a colourless, mobile liquid, the vapour of which is irritant to the mucous membrane. It reacts with potassium cyanide, and with sodium ethoxide yields a substance which reduces Fehling's solution.

The ketones described above on reduction by sodium in alcohol furnish the corresponding carbinols, and the following were thus prepared: cyclo*Propylpropylcarbinol*, $OH\cdot CHPr^{\alpha}\cdot CH<\begin{matrix}CH_2\\CH_2\end{matrix}$, D^{20} 0·8693, n_D^{20} 1·43663, b. p. 154—155°/750 mm., is a viscous, colourless liquid having a camphoraceous odour. The *acetate*, D^{20} 0·9013, b. p. 174—175°/764 mm., is colourless, mobile, and of agreeable piperaceous odour. cyclo*Propylbutylcarbinol*, D^{20} 0·8721, n_D^{20} 1·43984, b. p. 175°/751 mm., resembles its lower homologue; on saturation with hydrogen bromide it furnishes two monobromo-compounds, the one probably cyclo*propylbutylcarbinyl bromide*, b. p. 150°/40 mm., and the *other*, b. p. 120°/40 mm., probably an ethylenic compound derived from the dibromooctane, D^{20} 1·3145, n_D^{20} 1·48302, obtained when a mixture of the two monobromo-compounds is further treated with hydrogen bromide, the trimethylene ring being thereby opened (compare Dalle, Abstr., 1902, i, 525; Perkin, Abstr., 1902, i, 597; and Demjanoff and Fortunatoff, Abstr., 1907, i, 1033). cyclo*Propyl*-iso*butylcarbinol*, D^{20} 0·8648, n_D^{20} 1·43553, b. p. 167°/751 mm., is viscous and possesses a camphoraceous odour. cyclo*Propylethylpropyl*-*carbinol*, $OH\cdot CEtPr^{\alpha}\cdot CH<\begin{matrix}CH_2\\CH_2\end{matrix}$, D^{20} 0·8843, n_D^{20} 1·45147, b. p. 178—179°/735 mm., obtained by the action of magnesium ethyl bromide on *cyclo*propyl propyl ketone, is a strong smelling liquid. It yields a *bromide*, b. p. 298°/739 mm. (decomp.), which on treatment with potassium hydroxide in alcohol at 150° furnishes a mixture of

hydrocarbons, D^{20} 0·7894, n_D^{20} 1·43737, b. p. 147—149°/757 mm. (compare Bruylants, *loc. cit.*).

*cyclo*Propylcarbinol is readily esterified by hydrogen bromide in the cold, and from the resulting bromide may be obtained, by treatment with sodium iodide in methyl alcohol, the iodide, which with potassium hydroxide in alcohol gives (1) a small yield of a *hydrocarbon*, possibly $CH{:}CH{<}\begin{matrix}CH_2\\CH_2\end{matrix}$ or $\begin{matrix}CH_2{\cdot}CH\\ \|\\ CH_2{\cdot}CH\end{matrix}$ (compare Demjanoff, Abstr., 1908, i, 85) b. p. −3° to 1°, which combines with bromine to form a tetra bromide, $CH_2Br{\cdot}CHBr{\cdot}CHBr{\cdot}CH_2Br$ (?), m. p. 112—114°, and (2) cyclo*propylcarbinyl ethyl ether*, $OEt{\cdot}CH_2{\cdot}CH{<}\begin{matrix}CH_2\\CH_2\end{matrix}$, b. p. 98—101°, a liquid of ethereal odour. With dry potassium hydroxide, but little action occurs, and the ether appears to be the chief product. *cyclo*Propylcarbinyl iodide differs markedly from the isomeric *iso*butyl iodide in its behaviour with potassium hydroxide in alcohol, and similarly, whilst *iso*butyric chloride is readily chlorinated, the chloride of *cyclo*propylcarboxylic acid is recovered practically unchanged after treatment with chlorine. T. A. H.

Action of Hydrazine Hydrate on 1-Methyl*cyclo*hexan-3-one. A. MERKIN (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1204—1211).—When 1-methyl*cyclo*hexan-3-one is treated with hydrazine hydrate, it yields (1) the ketazine, $C_7H_{12}{:}N{\cdot}N{:}C_7H_{12}$, b. p. 229°/140 mm., 210°/71 mm., α −51·59° to −45·84°; (2) 1-*methyl*cyclo*hexan-3-one hydrazone*, $CH_2{<}\begin{matrix}CHMe{\cdot}CH_2\\CH_2{-}{-}CH_2\end{matrix}{>}C{:}N{\cdot}NH_2$, b. p. 154°/71 mm., D_0^{15} 0·9603, n_D^{15} 1·5043, $[\alpha]_D$ −35·94°. It is a colourless liquid, which decomposes and turns yellow in air, forms the above ketazine on distillation, and combines with water, forming a crystalline *hydrate*. With benzaldehyde it forms benzaldazine, m. p. 93°, and methyl*cyclo*hexanone, and when reduced with sodium and alcohol, it yields aminomethyl*cyclo*hexane and *methyl*cyclo*hexylmethylcyclohexylidenehydrazine*,

$$C_7H_{12}{:}N{\cdot}NH{\cdot}C_7H_{13},$$

which with hydrochloric acid yields methyl*cyclo*hexylhydrazine hydrochloride, $C_7H_{13}{\cdot}NH{\cdot}NH_2,HCl$; the free hydrazine has b. p. 208—209°.

The thiosemicarbazide, $NHPh{\cdot}CS{\cdot}NH{\cdot}NH{\cdot}C_7H_{13}$, m. p. 135°, crystallises from methyl alcohol in needles and in rhombic plates, $[\alpha]_D$ −15·94°. By treating methyl*cyclo*hexylhydrazine with pyruvic acid in hydrochloric acid solution, prismatic crystals of the *hydrazone*,

$$C_7H_{13}{\cdot}NH{\cdot}N{:}CMe{\cdot}CO_2H,$$

m. p. 96—98°, $[\alpha]_D$ −16·62° are produced, together with a *substance*, m. p. 236—237°, $[\alpha]_D$ −11·05°, which is also obtained by treating the hydrazine with hydrochloric acid, and when heated with fuming hydrochloric acid in a sealed tube at 180° is partly converted into a gelatinous mass soluble in alkalis. The methyl*cyclo*hexylhydrazine re-obtained from the methyl*cyclo*hexylhydrazone of pyruvic acid yields a *thiosemicarbazide*, m. p. 135—136°, $[\alpha]_D$ −23·68°, showing that the original hydrazine consists of a mixture of stereoisomeric hydrazines.

The ketazine, $C_7H_{12}{:}N_2{:}C_7H_{12}$, when treated with hydrazine hydrate

and solid potassium hydroxide on a water-bath, is partly converted into *1-methylcyclohexan-3-onehydrazone*. Z. K.

Compounds of Aluminium Chloride and Bromide with Acetophenone and Benzophenone. BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 1298—1307).—Aluminium bromide reacts more readily with benzophenone than does the chloride. It forms a crystalline, molecular compound, $AlBr_3,COPh_2$, m. p. 142°, which is instantly decomposed by water, with formation of benzophenone. The solubility curve of the two substances is very similar to those obtained for aluminium bromide with the nitro-derivatives of aromatic hydrocarbons and their derivatives (Abstr., 1909, *i*, 900; 1910, i, 234). It has two eutectic points, at 38° and composition $AlBr_3,4{\cdot}51COPh_2$, and at the same temperature but composition $AlBr_3,0{\cdot}49COPh_2$. Aluminium chloride also forms a molecular compound, $AlCl_3,COPh_2$, m. p. 130° (Perrier gives 119°). The solubility curve has two eutectic points, at 39·5° and composition $AlCl_3,4{\cdot}92COPh_2$, and at 60° at the composition $AlCl_3,0{\cdot}57COPh_2$. When working with these substances it is best to use no third substance, such as sulphuric acid, as solvent. Aluminium halides with acetophenone also yield molecular compounds, but the system is difficult to investigate, since the salts crystallise very slowly, and readily yield resinous products.

Curves and tables are given. Z. K.

Organic Syntheses by means of Sunlight. V. Behaviour of Acids and Ethers [including Esters] with Benzophenone. EMANUELE PATERNÒ and G. CHIEFFI (*Gazzetta*, 1910, 40, ii, 321—331. Compare Abstr., 1909, i, 240; 1910, i, 41).—Acetic acid and benzophenone do not react when exposed to sunlight. Propionic acid and benzophenone yield a small quantity of a yellow, resinous acid *substance*. Benzophenone and butyric acid give benzopinacone and a yellow *resin*, m. p. 74—75°, which has the properties of an acid, and contains both benzophenone and butyric acid groups. Between benzophenone and benzoic acid no reaction occurs. Phenylacetic acid and benzophenone yield benzopinacone and *β-hydroxy-αββ-triphenylpropionic acid*, $OH{\cdot}CPh_2{\cdot}CHPh{\cdot}CO_2H$, which forms small, flat needles, m. p. 205—208°. The *silver* salt was prepared. Phenylpropionic acid and benzophenone give benzopinacone, an *acid*, m. p. 271—273°, and a substance, m. p. 161—163°. These two products, however, contain traces of benzopinacone. The acid has the formula $C_{18}H_{18}O_4$, and is either diphenyladipic acid,

$$CO_2H{\cdot}CH_2{\cdot}CHPh{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2H,$$

or dibenzylsuccinic acid. It resists boiling with nitric acid, and does not decolorise permanganate. The substance of m. p. 161—163° has the formula $C_{22}H_{18}O_2$, and is probably the *lactone*,

$$\begin{matrix} CH_2 & \text{---} & CO \\ | & & \\ CHPh{\cdot}CPh_2 & & \end{matrix}\!\!>O.$$

Benzophenone reacts with ethyl ether, producing benzopinacone and a *resin*, $C_{17}H_{18}O_2$, which in the authors' opinion probably has the structure $CPh_2\!<\!\begin{matrix} O \\ CH_2 \end{matrix}\!>\!CH{\cdot}OEt$, although owing to the difficulty of

purifying the substance some of the analytical results do not agree very well with that formula. Benzophenone and *iso*amyl ether yield benzopinacone, a heavy, viscous *oil*, the analysis of which agrees with the formula $C_{28}H_{32}O_2$ required by a product analogous to that from ethyl ether. Acetal and benzophenone give benzopinacone and a heavy *oil*. Glycerol dimethyl and diethyl ethers behave similarly. Amyl formate and benzophenone yield benzopinacone and a heavy, viscous oil, which appears to be a *lactone* analogous to that obtained from phenylpropionic acid. The formation of benzopinacone was also observed when benzophenone was kept in sunlight with ethyl acetate, ethyl ethylmalonate, ethyl tartrate, the methyl ethers of *m*-cresol, *p*-cresol and resorcinol, and with ethyl phenylpropionate. In most cases the formation of resinous substances was also noted. Benzophenone and benzyl acetate yield in addition to benzopinacone, a *substance*, m. p. 218—219° (compare following abstract). R. V. S.

Organic Syntheses by means of Sunlight. VI. The Product of the Reaction between Benzophenone and Benzyl Acetate. Emanuele Paternò and G. Forlì-forti (*Gazzetta*, 1910, 40, ii, 332—341. Compare preceding abstract).—The substance forms small, hard, colourless crystals, and has the formula, $C_{22}H_{20}O_2$, of an additive product of equimolecular quantities of benzophenone and benzyl acetate. The authors ascribe to it the structure of the *acetyl* derivative of *triphenylethylene glycol*, $OH\cdot CPh_2\cdot CHPh\cdot OAc$, and advance the following reasons in support of this formula: (1) when the substance is heated with alcoholic potassium hydroxide, benzhydrol, benzoic acid, and acetic acid are formed; (2) when heated with alcohol in a sealed tube at 200° for eight hours, the compound yields ethyl acetate and a substance, $C_{20}H_{14}O$, m. p. 134—135°, apparently identical with triphenylvinyl alcohol (Biltz, Abstr., 1899, i, 439), which is a product of dehydration of triphenylethylene glycol; (3) by the action of acetyl chloride on the substance, triphenylvinyl alcohol is obtained, whilst acetyl chloride in presence of acetic acid leads to the formation of a *substance* crystallising in needles, m. p. 103—105°, which has the composition of an acetyl derivative of that alcohol.

R. V. S.

Some Properties of Piperonyloin. Henry A. Torrey and J. B. Sumner (*J. Amer. Chem. Soc.*, 1910, **32**, 11, 1492—1494).—The piperonyloin was prepared by Perkin's method (Trans., 1891, 59, 150), some modifications being introduced. A comparison was made of the behaviour of piperonyloin and of benzoin under similar conditions, and it was found that piperonyloin is much less reactive than benzoin; thus it is not affected by reducing agents or acetyl chloride, and it does not form an oxime. The only substances found with which it reacts easily are carbamide and ammonium thiocyanate. *Piperonyloincarbamide*, $C_{17}H_{12}O_5N_2$, forms pale pink crystals, decomposing at 265°. The *thiocarbamide* crystallises in long, felted, nearly white needles, decomposing at 260°, and probably has the formula $C_{17}H_{12}O_4N_2S$. N. C.

Allyloxanthranol and Some of its Derivatives. H. KONDO (*Ber.*, 1910, **43**, 3182—3187).—The investigation was undertaken with the object of preparing benzanthrone (Bally, Abstr., 1905, i, 237).

9-*Allyloxanthranol*, $CO<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>C(OH)\cdot C_3H_5$, is prepared in a similar manner to amyloxanthranol (compare Liebermann, Abstr., 1882, 855; Liebermann and Roka, Abstr., 1908, i, 427) by the action of allyl bromide on anthraquinone. It crystallises in large, colourless, measurable crystals, m. p. 108°. On reduction with sodium amalgam, 9-propyloxanthranol, m. p. 164° (Hallgarten, Abstr., 1889, 894), is formed.

With hydrogen bromide, 9-*β-bromopropyloxanthranyl bromide*, $CO<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CBr\cdot CH_2\cdot CHBrMe$, is obtained in colourless, prismatic crystals, m. p. 129°. With bromine in carbon disulphide solution, 9-*αβ-dibromopropyloxanthranol*, $CO<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>C(OH)\cdot C_3H_5Br_2$, is obtained; it crystallises in colourless, slender prisms, m. p. 147°.

The elimination of hydrogen bromide from the dibromide is incomplete in presence of pyridine and quinoline. With alcoholic potassium hydroxide, heat is required to render it complete, and decomposition products are readily formed. On the addition of acid, a compound, $C_{17}H_{12}O_2$, possibly allylenyloxanthranol, is obtained of a faint yellow hue, m. p. 111°. It gives a green coloration with concentrated sulphuric acid. With bromine in carbon disulphide, a small quantity of a blood-red, crystalline precipitate is formed, which is very easily decomposed, becoming yellow. With dilute alkali hydroxides, a yellow potassium salt is obtained, which fluoresces like eosin in alcoholic solution.

From the carbon disulphide mother liquors a yellow compound, 9-*dibromomethyleneanthrone*, $CO<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>C:CBr_2$, m. p. 167°, is obtained, which is quantitatively converted into anthraquinone by moisture.

E. F. A.

Some Derivatives of 2-Acetyl-α-naphthol. HENRY A. TORREY and E. J. CARDARELLI (*J. Amer. Chem. Soc.*, 1910, **32**, ii, 1477—1488).—2-Acetyl-α-naphthol was prepared by Friedländer's method (Abstr., 1895, i, 668), and various derivatives obtained and examined. During experiments on the action of benzaldehyde on 2-acetyl-α-naphthol, a second form of 2-acetyl-α-naphthol was obtained in brown plates, m. p. 98°, instead of the original yellowish-green needles, m. p. 103°. It is thought that the brown form has a quinonoid structure, and that the yellow form is the phenol. Several methods were tried, unsuccessfully, to obtain a quinoline from 2-acetyl-α-naphthol.

4-Amino-2:(*t*)-diacetyl-α-naphthol forms yellowish-white needles, arranged like chestnut burs, and melting at 212°. Friedländer gives m. p. 107° for this compound, but the authors could not obtain this melting point.

4-Amino-2-acetyl-α-naphthol reacts quantitatively with aldehydes;

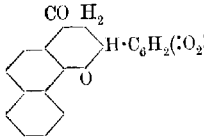
4-benzylideneamino-2-acetyl-α-naphthol forms plates between the colour of brass and bronze, m. p. 159°; the corresponding *piperonylidene* derivative crystallises in brown plates, m. p. 178°, and the *cinnamylidene* derivative in brownish-yellow needles, m. p. 144°.

4-Nitro-2-cinnamoyl-α-naphthol, $OH{\cdot}C_{10}H_5(NO_2){\cdot}CO{\cdot}CH{:}CHPh$, crystallises in two forms, a yellow one and a red one; the melting point varies from 202° to 208°. *2-m-Nitrocinnamoyl-α-naphthol* forms red, microscopic needles, m. p. 210°; it absorbs bromine easily, forming a vermilion-coloured substance. By the action of sodium hydroxide on a mixture of 2-acetyl-α-naphthol and 6-nitropiperonal, the ketol, *2-(β-hydroxy-β-6′-nitropiperonylpropionyl)-α-naphthol*,

$$CH_2O_2{:}C_6H_2(NO_2){\cdot}CH(OH){\cdot}CH_2{\cdot}CO{\cdot}C_{10}H_6{\cdot}OH,$$

is obtained. It forms lemon-yellow needles, m. p. 201—202°.

The *monoacetate* of the ketol crystallises in cream needles, m. p. 188—190°; it forms a *tribromo*-derivative. The *diacetate* of the ketol forms golden, rectangular crystals, m. p. 197—198°. By the action of bromine on the ketol, two *substances* are obtained, one red, m. p. 252°, and one yellow, m. p. 220°.



2-(6-*Nitropiperonyl*)-*naphthaflavanone* (annexed formula) crystallises in red needles with an orange tinge, m. p. 226°; bromine acts on it to give the *substance*, $C_{20}H_{12}O_6NBr$, which forms an orange powder decomposing at 250—255°.

N. C.

Some Derivatives of Hydroxyquinol. I. and II. Guido Bargellini and Ghersch Avrutin (*Gazzetta*, 1910, 40, ii, 342—347, 347—353. Compare Reigrodski and Tambor, Abstr., 1910, i, 578).—I. In some of their results the authors have been anticipated by the publication cited above. 2 : 4 : 5-Trimethoxyacetophenone has b. p. 285—290°/33 mm. When oxidised with permanganate, it yields asaronic acid. Its *oxime* forms colourless crystals, m. p. 126—127°. The *semicarbazone* crystallises in small laminæ, m. p. 186—188°. 2 : 4 : 5-Trimethoxychalkone has m. p. 117—118° (Reigrodski and Tambor gave 113—114°). *4 : 2′ : 4′ : 5′-Tetramethoxychalkone* (from trimethoxyacetophenone and anisaldehyde) crystallises in small, yellow needles, m. p. 123—124°, and dissolves in concentrated sulphuric acid, producing an intense red coloration. *3 : 4 : 2′ : 4′ : 5′-Pentamethoxychalkone* (from veratraldehyde) forms yellow scales, m. p. 155°, and gives a red coloration when dissolved in concentrated sulphuric acid. *3 : 4-Methylenedioxy-2′ : 4′ : 5′-trimethoxychalkone* (from piperonaldehyde) crystallises in yellow laminæ, m. p. 182—183°. It gives a reddish-violet coloration with concentrated sulphuric acid.

II. When triacetylhydroxyquinol is heated with acetic acid and zinc chloride, or with chloroacetic acid and zinc chloride, or with zinc chloride alone, a mixture of two substances is obtained, namely, a red *compound*, crystallising in needles, m. p. 200—202° (decomp.), and a colourless *substance*, crystallising in silvery scales, m. p. 165—166°. Both have the composition $(C_2H_2O)_n$, which agrees with that of

trihydroxyacetophenone and its three acetyl derivatives. Both substances yield trimethoxyacetophenone when treated with methyl sulphate. R. V. S.

Turmeric Oil. II. **Oxidation Products of Curcumone.** Hans Rupe and A. Steinbach (*Ber.*, 1910, **43**, 3465—3471. Compare Rupe, Lucksch, and Steinbach, Abstr., 1909, i, 598).—Potassium permanganate is the only oxidising agent which, by its attack on curcumone, gives some insight into the constitution of the ketone. When curcumone is treated with 4% potassium permanganate at the ordinary temperature, *p*-tolyl methyl ketone, terephthalic acid, and *p*-acetylbenzoic acid are produced. When curcumone is shaken for eight hours with aqueous sodium hypobromite at 0° in a bottle protected from light, a considerable quantity of the ketone is recovered unchanged, together with bromoform and an *acid*, $C_{12}H_{16}O_2$, m. p. 33—34°, b. p. 168—170°/12 mm., $[\alpha]_D^{20}$ 31·15° in alcohol, which is purified best through the *calcium* salt, $Ca(C_{12}H_{15}O_2)_2,3H_2O$; it receives the name *curcumic acid*, and is apparently identical with Jackson and Menke's turmeric acid. A small quantity of another *acid*,

$$C_{12}H_{16}O_3(?),$$

m. p. 150—151°, has also been isolated, which is oxidised to terephthalic acid by potassium permanganate. The oxidation of curcumic acid by 4% potassium permanganate in the presence of sodium carbonate at 0° yields *p*-tolyl methyl ketone, terephthalic acid, and a dibasic *acid*, $C_{12}H_{14}O_4$, m. p. 226—228°, which may be identical with Jackson and Menke's *apo*turmeric acid, m. p. 221°.

The preceding results indicate that curcumone, $C_{13}H_{18}O$, is a derivative of benzene containing two para-substituents, one of which is methyl, and the second, one or other of the groups

·CHMe·CH_2·CH_2·COMe,

·CHMe·CHMe·COMe, or ·CMeEt·COMe. Curcumic acid contains a carboxyl group in the place of the group ·COMe. C. S.

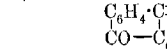
Dianilino-*p*-benzoquinoneanil. William Küster (*Ber.*, 1910, **43**, 2962—2964).—The compound obtained by Küster and Fuchs (Abstr., 1907, i, 572) by the action of aniline on hæmin is now shown to be dianilino-*p*-benzoquinoneanil and to be free from iron. Apparently hæmin acts as a ferric salt, and brings about to some extent the oxidation of aniline at the ordinary temperature. E. F. A.

Nitranilic Acid [3 : 6-Dinitro-2 : 5-dihydroxy-*p*-benzoquinone]. Rudolf Nietzki (*Ber.*, 1910, **43**, 3457—3459).—Potassium nitroanilate is obtained in 75—80% yield by adding the paste, obtained by stirring quinol with acetic anhydride and a few drops of concentrated sulphuric acid, to cold nitric acid, D 1·48, adding subsequently concentrated sulphuric acid, and pouring the mixture, after being kept for twelve hours at 0°, on to ice; the solid product is treated with ice and potassium hydroxide (compare Henle, *Annalen*, 1906, **350**, 334). C. S.

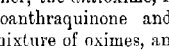
Action of **Hydroxylamine on Some Ortho-substituted Derivatives of Anthraquinone.** Martin Freund and Fritz Achenbach (*Ber.*, 1910, **43**, 3251—3260).—*o*-Chlorinated anthra-

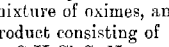
quinones react with hydroxylamine more readily than anthraquinone itself, and the oximes formed lose hydrogen chloride when boiled with alkali, yielding cyclic compounds resembling those prepared by Meyer and Cathcart from *o*-halogenated benzophenones (Abstr., 1892, 992; 1893, i, 94).

1-Chloroanthraquinone reacts with hydroxylamine hydrochloride and alcohol at 180°, yielding a mixture of two oximes, but when these are boiled with dilute sodium hydroxide solution, the one, presumably the *syn*-compound, is transformed into anthrone*iso*oxazole,



whereas the other, the *anti*oxime, is not decomposed.

1 : 5-Dichloroanthraquinone and hydroxylamine hydrochloride at 185° yields a mixture of oximes, and when these are boiled with alkali, an insoluble product consisting of a mixture of 5-chloro-10-anthrone-1 : 9-*iso*oxazole,  , and anthradi*iso*oxazole,



is formed together with two oximes which remain dissolved in the alkali; these are the *anti*-forms of the mono- and di-oximes of 1 : 5-dichloroanthaquinone.

*Anthrone*isoo*xazole*, $C_{14}H_7O_2N$, crystallises from hot chlorobenzene in slender, nearly colourless needles, m. p. 298·5°. 1-*Chloroanthraquinone*-anti-*monoxime*, $C_{14}H_8O_2NCl$, crystallises from a mixture of methyl alcohol and water in golden-yellow plates, m. p. 219—222° (decomp.). 1 : 5-*Dichloroanthraquinone*-anti-*monoxime*, $C_{14}H_7O_2NCl_2$, crystallises from hot glacial acetic acid in yellow needles, m. p. 252° after sintering at 235°.

1:5-*Dichloroanthraquinone*-anti-anti-*dioxime*, $C_{14}H_8O_2N_2Cl_2$, is, unlike the monoxime, insoluble in hot chlorobenzene, and forms a grey powder, m. p. 245° (decomp.).

1-*Chloroanthrone*isoo*xazole*, $C_{14}H_6O_2NCl$, crystallises from glacial acetic acid, and has m. p. 229° after sintering at 225°. *Anthraliso-oxazole*, $C_{14}H_6O_2N_2$, is sparingly soluble in hot chlorobenzene, and has m. p. 304°.

1-*Methoxyanthraquinonemonoxime*, $C_{15}H_{11}O_3N$, crystallises from alcohol in dark brown needles, m. p. 198°. The corresponding 1-*phenoxy*-derivative, $C_{20}H_{13}O_3N$, crystallises from 75% acetic acid in brown needles, m. p. 175° after sintering at 155°.

The *monoxime* of anthrarufin dimethyl ether, $C_{16}H_{13}O_4N$, has m. p. 196° after sintering at 185°. J. J. S.

Action of Bornyl Chloride on Aromatic Amines. Fritz Ullmann and Alfred Schmid (*Ber.*, 1910, **43**, 3202—3209).—Bornyl chloride reacts with primary aromatic amines, yielding a mixture of camphene and bornylarylamine.

Bornylaniline, $C_{10}H_{17}\cdot NHPh$, obtained by boiling a mixture of bornyl chloride and aniline for three hours, is a colourless, strongly refractive, viscid liquid, b. p. 140°/2 mm., and forms a *hydrochloride*,

m. p. 198°, and an *acetyl* derivative, m. p. 123°. On nitration, the latter yields *acetobornyl-p-nitroanilide*, $C_{10}H_{17}\cdot NAc\cdot C_6H_4\cdot NO_2$, white, glistening leaflets, m. p. 185°.

Acetylbornyl-p-phenylenediamine, $C_{10}H_{17}\cdot NAc\cdot C_6H_4\cdot NH_2$, obtained by reducing the nitro-compound with stannous chloride and hydrochloric acid, crystallises in colourless needles, m. p. 148°.

When bornyl chloride is boiled with aniline and the product distilled under ordinary pressure, a 96% yield of camphene is obtained.

Bornyl-o-toluidine, $C_{10}H_{17}\cdot NH\cdot C_6H_4\cdot Me$, prepared from bornyl chloride and *o*-toluidine, crystallises in needles, m. p. 55°, b. p. 160°/1 mm.; the *hydrochloride* has m. p. 180°.

Bornyl-p-toluidine has b. p. 162°/3 mm., crystallises in needles, m. p. 33°, and yields a crystalline *hydrochloride*, m. p. 214° (decomp.).

Bornyl-m-4-xylidine, b. p. 176°/7 mm., crystallises from methyl alcohol in large needles, m. p. 79°.

The action of bornyl chloride on *m*-tolylenediamine leads to the formation of camphene and *diamino-ditolylamine*, $C_{14}H_{17}N_3$, glistening, colourless leaflets, m. p. 154—155°.

The same product is obtained by heating *m*-tolylenediamine with its hydrochloride at 200°. The *diacetyl* derivative, has m. p. 247°.

F. B.

Catalytic Reduction. III. Aladar Skita and H. Ritter (*Ber.*, 1910, **43**, 3393—3399. Compare Abstr., 1908, i, 855; 1909, i, 479).—*d*-Pulegone is reduced by hydrogen under two atmospheres pressure, in presence of colloidal platinum, to *d*-menthone, whilst the product obtained with other reducing agents is *l*-menthone (Beckmann, Abstr., 1889, 721). Phorone yields di*iso*butylcarbinol, whilst mesityl oxide is only reduced to methyl *iso*butyl ketone. This difference may be explained by the different positions of the carbonyl group.

Using a lower pressure of hydrogen (one and a-half atmospheres), phorone may be reduced only to valerone, whilst under as high a pressure as five atmospheres it may be reduced to methyl*iso*butylcarbinol. *iso*Phoroneoxime yields, under four atmospheres, 5-amino-1:1:3-trimethyl*cyclo*hexane.

Phenylacetaldehyde is converted into phenylethyl alcohol, and quinone into quinol.

C. H. D.

Action of Hydrazine Hydrate on Thujone. Nicolai M. Kizner (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1198—1204).—By the action of an excess of hydrazine hydrate on thujone in alcoholic solution, the latter is converted quantitatively into *thujonehydrazone*, $CH_2<\begin{matrix}CH\cdot CHMe\\ |\\ CPr—CH_2\end{matrix}>C:N\cdot NH_2$, a colourless liquid with a faint odour, b. p. 149°/35 mm., D_0^{20} 0·9504, n_D^{20} 1·4952, $[\alpha]_D$ +123·75°, which readily reduces ammoniacal silver oxide, and dissolves in hydrochloric acid with formation of thujone, b. p. 202—203·5°/739 mm., α +33·36°; the original thujone had α +65·0°. When reduced with sodium in alcoholic solution, the hydrazone yields *thujylhydrazine*, $C_{10}H_{17}\cdot NH\cdot NH_2$, b. p.

142—144°/38 mm., 242—244°/741 mm., D_0^{20} 0·9302, $[\alpha]_D$ +76·67°, n_D^{20} 1·4800, which is oxidised on exposure to air and reduces ammoniacal silver oxide. Thujone, b. p. 202—204°/739 mm., α +26·28°, and impure thujylamine, b. p. 196—199°, α +50·30°, are formed as by-products. When mixed with phenylthiocarbimide, the hydrazone forms the *phenylthiosemicarbazide*, $NHPh\cdot CS\cdot NH\cdot NH\cdot C_{10}H_{17}$, which forms prismatic needles, m. p. 134·5—135°, $[\alpha]_D$ +51·89° in chloroform solution, whilst with potassium ferricyanide in potassium hydroxide solution the hydrazine yields thujene, b. p. 157·5—158°/741 mm., D_0^{20} 0·8164, n_D^{20} 1·4398, $[\alpha]_D$ +53·41°. Thujene has a faint odour, and reacts very slowly with alkaline potassium permanganate. In chloroform solution it absorbs bromine, forming an unstable *bromide*; it also combines with hydrogen bromide, forming a heavy *bromide*, which when boiled with potassium hydroxide yields an unsaturated *hydrocarbon*, $C_{10}H_{18}$, b. p. 162—165°, D_{20}^{20} 0·8139, n_D^{20} 1·4512, α +3·32°.

Z. K.

Semicarbazide and Cyclic Nitrosochlorides. Hans Rupe and H. Altenburg (*Ber.*, 1910, 43, 3471—3474).—The ease with which the semicarbazide group replaces the oximino-group in aliphatic oximino-ketones (Rupe and Kessler, Abstr., 1910, 93) has induced the authors to examine the behaviour of some cyclic nitrosochlorides. An alcoholic solution of *d*-β-bislimonene nitrosochloride is boiled for one hour with a concentrated aqueous solution of semicarbazide hydrochloride. When the product is distilled directly with steam, carvone is obtained, but when the product is first neutralised by sodium hydrogen carbonate and is then distilled with steam, the oxime and the semicarbazone of carvone are obtained. Bisterpineol nitrosochloride, under similar conditions, yields terpineol by direct distillation with steam, the residue containing 8-hydroxydihydrocarvonesemicarbazone. The latter, together with hydrazodicarbonamide, is obtained when potassium acetate is added to the aqueous-alcoholic solution before boiling.

l-Carvoxime is produced when the product of the reaction between magnesium and *d*-limonene nitrosochloride in dry ether is decomposed by cold water and dilute sulphuric acid.

C. S.

Hydrogenation of Isomeric Thujenes and of Sabinene. Thujane. Leo A. Tschugaeff and W. Fomin (*Compt. rend.*, 1910, 151, 1058—1062. Compare Abstr., 1905, i, 71).—Zelinsky (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 768) has shown that reduction of *l*-α-thujene by Sabatier and Senderens' method leads to rupture of the trimethylene ring and production of a hydrocarbon, $C_{10}H_{20}$. When the reduction, however, is effected at the ordinary temperature by hydrogen and platinum-black, *thujane*, $C_{10}H_{18}$, is obtained; this has b. p. 157°/758 mm., D_4^{15} 0·8161, n_D^{20} 1·43759, $[\alpha]_D$ +62·03°. When prepared from *d*-β-thujene, the product has b. p. 157°/759 mm., D_4^{18} 0·8191, n_D^{18} 1·44102, $[\alpha]_D$ +34·72°, whilst under the same conditions sabinene gives a hydrocarbon, b. p. 157—158°/760 mm., D_4^{17} 0·8190, n_D^{17} 1·44393, $[\alpha]_D$ +18·56°. The hydrocarbons are probably identical, except in their

optical rotations, and their stability towards oxidising agents suggests that they have the constitution $CH_2<\begin{matrix}CH-CHMe\\ |\\ CPr^{\beta}-CH_2\end{matrix}>CH_2$.

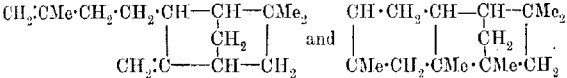
W. O. W.

Constituents of Ethereal Oils. Regeneration of Caryophyllene. FRIEDRICH W. SEMMLER and ERWIN W. MAYER (*Ber.*, 1910, 43, 3451—3455. Compare Schreiner and Kremers, Abstr., 1902, i, 108; Schimmel & Co., *Bericht*, October, 1910, 173).—By the elimination of hydrogen chloride from caryophyllene dihydrochloride by means of a saturated methyl-alcoholic solution of potassium hydroxide or a concentrated solution of sodium methoxide, a hydrocarbon is obtained with the following properties: b. p. 121—122·5°/12 mm., D_4^{20} 0·8996, α_D +19°, n_D^{20} 1·4990. This hydrocarbon yields the same dihydrochloride, m. p. 69—70°, as is obtained from the original caryophyllene. Both dihydrochlorides are dextrorotatory, although the natural hydrocarbon is lævo- and the regenerated hydrocarbon dextro-rotatory. The conclusion is drawn that the natural hydrocarbon contains the same caryophyllene as the regenerated, but contains, in addition, a lævorotatory compound (compare Deussen and Lewinsohn, Abstr., 1908, i, 353; 1909, i, 171).

The products obtained by eliminating the hydrogen chloride by means of dilute alkalis or of sodium acetate and acetic acid are not homogeneous. When, however, the dihydrochloride is boiled for three-quarters of an hour with quinoline, an isomeric caryophyllene with the following properties is obtained: b. p. 122—123°/13 mm., D_4^{20} 0·927, n_D^{20} 1·50246, and α_D^{20} −57° in a 1-dcm. tube.

This hydrocarbon is regarded as the pure tricyclic caryophyllene.

The following formulæ are suggested:



Recovered caryophyllene. and Tricyclic caryophyllene.

J. J. S.

Philippine Terpenes and Essential Oils. IV. RAYMOND F. BACON (*Philippine J. Sci.*, 1910, 5, 257—265. Compare Abstr., 1909, i, 658).—The volatile oils from a number of plants indigenous to, or cultivated in, the Philippines are described.

Cinnamomum mindanaense bark furnishes a yellow oil, D_{30}^{30} 0·960, n_D^{30} 1·5300, α_D^{30} +7·9°, containing 60% of an aldehyde, and having a strong odour of cinnamon. *Canarium villosum* yields an oleo-resin, which on distillation furnishes about 11% of oil, distilling mainly between 154° and 180°, and containing pinene and dipentene. Native grown ginger-root furnished 0·072% of a pale yellow oil, D_{30}^{30} 0·8850, n_D^{30} 1·4830, α_D^{30} +5·9°, and saponification number 14; this had an odour similar to that of orange-peel oil, and was completely soluble in two or more volumes of 90% alcohol. *Ocimum sanctum* leaves gave 0·6% of greenish-coloured oil, having α_D^{30} 0, n_D^{30} 1·5070, D_{30}^{30} 0·952, and saponification value 2·8. It had an anise-like odour, and the fraction boiling at

85—95°/9 mm. gave homoanisic acid on oxidation. *Curcuma Zedoaria* roots furnished 0·065 to 0·25% of brown oil, D_4^{30} 0·933, n_D^{30} 1·4920 to 1·5070, α_D^{30} + 1°10′, saponification value 2, and soluble in two or more volumes of 80% alcohol. The oil boiled from 60° to 166°/7 mm., and the higher fractions contained a sesquiterpene alcohol, D_{30}^{30} 1·01, m. p. 67°, b. p. 160°/7 mm., which appears to be the chief odoriferous constituent of the oil, and to belong to the tricyclic group. It gave a deep red colour with sulphuric acid. Turmeric roots furnished a brownish-coloured oil, having D_{30}^{30} 0·390, n_D^{30} 1·5030, α_D^{30} + 8·6°, ester number 81, and miscible with 75% or stronger alcohol in all proportions (compare Rupe, Luksch, and Steinbach, Abstr., 1909, i, 598). The yellow flowers of *Michelia champaca* furnished 0·2% of oil, which when kept, deposited (1) a crystalline solid, (2) an amorphous solid. The residual brown oil so obtained had D_{30}^{30} 0·9543—1·020, n_D^{30} 1·4550—1·4820, saponification number 160—180; that having the higher constants had the finer odour. It is considered likely that the reputed Manila champaca oils examined by previous investigators were not derived wholly from champaca flowers. T. A. H.

Essential Oil of Spanish Wild Marjoram. Bernabé Dorronsoro (*Anal. Fis. Quim.*, 1910, **8**, 315—328).—Spanish wild marjoram (*Mejorana silvestre, Thymus Mastichina*, L.) is distilled largely in the south and centre of Spain. Authentic samples of the oil taken in the years 1898–1909 gave values D_{15}^{25} 0·907—0·945, n_D^{25} 1·4630—1·4654, and α_D^{25} varying from − 1°40′ to + 9°20′ (200 mm. tube).

The saponification value of the oil had a range 12·7—18·5 with samples taken during the years 1898–1909; the esters calculated as linalyl acetate ranged from 4·44—6·47%; the acetylation number ranged from 29·2—45·6, and the alcohol, calculated as $C_{10}H_{18}O$, varied from 8·20—13·0. The analysis of a 5 kilogram sample gave the following result: *d*-pinene, 7—8%; cineol or eucalyptol, 64—72%; phenols, less than 0·1%; ketones, less than 0·1%; esters (as linalyl acetate), 4·44—6·47%, and free alcohols (linalool), 8·2—14·1%.

The remarkable point with regard to this oil is the production from a species of *Thymus* of a high proportion of cineol and the entire absence of thymol, cineolic acid, and methylheptenone; the oxidation products of cineol are also absent. W. A. D.

So-called Crystalline Chlorophyll—a Mixture. M. Tswett (*Ber.*, 1910, **43**, 3139—3141).—The green crystals of chlorophyll discovered by Borodin, and recently investigated by Willstätter, have been regarded (Tswett, Abstr., 1908, i, 669) either as a compound of the genuine chlorophyllins with possibly a third substance, or as an isomorphous mixture of two chlorophyllin derivatives. By means of the adsorption analysis of crystalline chlorophyll, dissolved in ether and diluted with ten volumes of light petroleum, the chromatogram is proved to show two zones—a superior greenish-yellow and an inferior greenish-blue. Accordingly, crystalline metachlorophyllin is an isomorphous mixture of α- and β-metachlorophyllins. E. F. A.

Di-ω-hydroxy-2 : 5-dimethylfuran. JAN J. BLANKSMA (*Rec. trav. chim.*, 1910, **29**, 403—406).—Although hexoses yield δω-hydroxymethylfurfuraldehyde when heated with oxalic acid, the author found that hexonic acids and the hexitols do not give di-ω-hydroxy-2 : 5-dimethylfuran under similar conditions. This substance may, however, be prepared by the action of sodium hydroxide on hydroxymethylfurfuraldehyde, hydroxymethylpyromucic acid being formed at the same time.

The crystals of *di-ω-hydroxy-2 : 5-dimethylfuran* are colourless, m. p. 80°; the *diacetyl* derivative forms colourless crystals, m. p. 64°.

The *semicarbazone* of hydroxymethylfurfuraldehyde crystallises in large, colourless crystals, m. p. 192°; its *p-bromophenylhydrazone* forms pale yellow crystals, m. p. 142°, which darken when exposed to sunlight. N. C.

Cyclic Sulphides. JULIUS VON BRAUN (*Ber.*, 1910, **43**, 3220—3226. Compare Abstr., 1910, i, 274).—The action of potassium sulphide on αζ-di-iodohexane yields only a very small quantity of hexamethylene sulphide, $(CH_2)_6S$, so that the tendency to the formation of the cyclic sulphides, $(CH_2)_nS$, diminishes progressively as n increases from 4 to 6.

If, however, two adjacent carbon atoms of a benzene ring are included in the chain, the formation of a cyclic sulphide containing a 6-membered ring takes place very readily; thus tetrahydrobenzthiopyran is produced in almost quantitative yield from *o*-ω-chloropropylthiophenol, $C_6H_4<^{[CH_2]_3Cl}_{SH}$.

It has been shown previously by the author (Abstr., 1910, i, 821) that the action of αζ-di-iodohexane on amines is accompanied by an isomerisation of the hexamethylene chain, the compounds produced containing the α-pipecoline ring and not a 7-membered ring. In order to determine if a similar transformation occurs in the formation of cyclic sulphides, the interaction of potassium sulphide and αδ-di-iodopentane has been investigated. The cyclic sulphide so obtained is different from that produced by the action of potassium sulphide on αε-di-iodopentane, so that no isomerisation of the pentamethylene chain has taken place in the latter reaction.

αδ-Di-iodopentane reacts vigorously with concentrated aqueous potassium sulphide in the presence of a little alcohol, yielding a *compound*, $C_{11}H_{18}O$, b. p. 229—230°, 122°/24 mm., and *2-methyltetrahydrothiophen*, $\begin{matrix}CH_2\cdot CHMe\\ |\\ CH_2---CH_2\end{matrix}>S$, b. p. 134°, a colourless liquid with a disagreeable odour, which yields a *methiodide*, crystallising in long, stout prisms, subliming at 172—173°, and transformed when kept in a desiccator into an amorphous, horny mass; the *platinichloride*, $(C_5H_{10}SMe)_2PtCl_6$, crystallises in reddish-yellow leaflets, m. p. 197° (decomp.).

The cyclic *sulphide*, $C_6H_{12}S$, is produced in a yield of 6% by the interaction of potassium sulphide and αζ-di-iodohexane in aqueous-alcoholic solution. It is a colourless oil, and gives a *methiodide*, crystallising in colourless needles, m. p. 147°.

The *platinichloride* crystallises from water in reddish-yellow leaflets, m. p. 193°.

The main product of the action of potassium sulphide on $\alpha\zeta$-di-iodohexane forms an *oil*, which solidifies on cooling, and probably consists of $I\cdot[CH_2]_6\cdot(S\cdot[CH_2]_6)_n\cdot S\cdot[CH_2]_6\cdot I$.

Thiochroman (*tetrahydrobenzthiopyran*), $C_6H_4<\begin{matrix}S\text{—}CH_2\\ |\\ CH_2\cdot CH_2\end{matrix}$, b. p. 128—130°/15 mm., is obtained as an almost odourless, pale yellow oil by the addition of potassium xanthate to a diazotised solution of *o*-ω-chloropropylaniline, slowly heating the *diazoxanthate*,

$$Cl\cdot[CH_2]_3\cdot C_6H_4\cdot N_2\cdot S\cdot CS\cdot OEt,$$

thus produced to 70°, and boiling the resulting dark-coloured *oil*, probably $Cl\cdot[CH_2]_3\cdot C_6H_4\cdot S\cdot CS\cdot OEt$, with alkali in aqueous-alcoholic solution. It does not react readily with methyl iodide, and on treatment with methyl sulphate yields a dark viscid, liquid *additive product*, which solidifies after several weeks' keeping.

Thiochromansulphone, $C_6H_4<\begin{matrix}SO_2\text{—}CH_2\\ |\\ CH_2\cdot CH_2\end{matrix}$, white crystals, m. p. 88·5°, is produced by oxidising thiochroman with potassium permanganate in aqueous solution. F. B.

Ephedrine and ψ-Ephedrine. Franz Wilhelm Calliess (*Apoth. Zeit.*, 1910, 25, 677—678).—Schmidt has shown previously (Abstr., 1908, i, 452) that when either of these bases is treated with hydrochloric acid at 100°, an equilibrium mixture of both is formed. It is now shown that ephedrine on acetylation is completely converted into ψ-ephedrine. The hydrochloride of either base on treatment with acetic anhydride yields an *acetyl* derivative, $C_{10}H_{14}ONAc,HCl$, m. p. 175°, $[\alpha]_D$ +26·7°, crystallising in colourless columns or tablets, which on hydrolysis by hydrochloric acid furnishes ψ-ephedrine. The *platinichloride* of the acetyl derivative, m. p. 184°, and the *aurichloride*, m. p. 165°, were prepared. T. A. H.

Components of Opium. Leopold van Itallie and Max Kerbosch (*Arch. Pharm.*, 1910, 248, 609—613).—Samples of opium from the Levant, India, China, America, France, Persia, and Egypt have been examined for the presence of morphine, narcotine, papaverine, thebaine, codeine, and narceine, the six commonest of the twenty-odd alkaloids in opium. The six alkaloids have been found in all of the samples except in the Indian opiums from Bengal, Patna, and Benares; these three do not contain papaverine. A reason for this peculiarity is being sought; it is not to be explained by difference in origin, because, as far as information is available, Bengal, Patna, and Benares opiums are obtained from the same plant, *Papaver somniferum* var. *album*, as Persian, Egyptian, Levantine, and other Indian opiums. C. S.

Action of Hydrogen Peroxide on Thebaine, Morphine, and their Ethers. Martin Freund and Edmund Speyer (*Ber.*, 1910, 43, 3310—3314).—When heated on the water-bath with 30%

hydrogen peroxide, thebaine, morphine, codeine, and dionine are converted into substances which are regarded as amine-oxides, since they are re-converted into the original alkaloids by sulphurous acid. They are characterised, however, by their stability towards acidified potassium iodide, and by their very slight physiological activity. *Thebaine oxide*, $C_{19}H_{21}O_4N$, m. p. about 80°, forms a *hydrochloride*, m. p. 238—239° (decomp.), colourless needles. *Morphine oxide*, $C_{17}H_{19}O_4N$, m. p. 274—275°, prismatic crystals, forms a *nitrate*, $C_{17}H_{19}O_4N,HNO_3,1\frac{1}{2}H_2O$, m. p. 206—208°, which loses water when heated, yielding a *substance*, $C_{34}H_{38}O_{13}N_4$, from which the hydrated nitrate is regenerated by crystallisation from water. *Codeine oxide*, $C_{18}H_{21}O_4N$, m. p. 230—231°, rectangular plates, forms a *nitrate*, m. p. 187°, and a *hydrobromide*, m. p. 196°. *Dionine oxide*, $C_{19}H_{23}O_4N$, m. p. 220—221°, felted needles, forms a *hydriodide*, which crystallises in elongated plates. C. S.

Narcotine and Hydrastine. PAUL RABE and ANDREW MCMILLAN (*Annalen*, 1910, **377**, 223—258).—A résumé of the development of the constitutional formulæ of hydrastine, narcotine, and narceine is given.

A proof is given that in Rabe's nornarceine (Abstr., 1907, i, 790) the carbonyl group is attached directly to the benzene nucleus; hence the same arrangement obtains in narceine itself (compare Freund and Oppenheim, Abstr., 1909, i, 410). The crude oximino-compound, m. p. 167—169°, obtained by treating nornarceine with alcoholic sodium ethoxide and ethyl nitrite, is suspended in chloroform at 0°, and converted by phosphorus pentachloride into hemipinic acid and 2-*cyano*-3-*methoxy*-4 : 5-*methylenedioxy*-1-*β*-*methylaminoethylbenzene*,

$$CH_2O_2{:}C_6H(OMe)(CN){\cdot}CH_2{\cdot}CH_2{\cdot}NHMe,$$

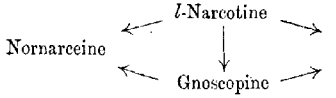
m. p. 61°, which forms a *hydrochloride*, m. p. 206—207° (decomp.), *picrate*, m. p. 168°, *picrolonate*, decomp. 232°, and a methiodide, m. p. 226°, identical with Freund and Oppenheim's compound (*loc. cit.*). In a similar manner, methylhydrasteine forms an *oximino*-compound,

$$C_{22}H_{24}O_8N_2,$$

m. p. 189—190°, which is converted by phosphorus pentachloride into hemipinic acid and 2-*cyano*-4 : 5-*methylenedioxy*-1-*β*-*dimethylaminoethylbenzene*, $CH_2O_2{:}C_6H_2(CN){\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2$, which forms a *picrate*, m. p. 188—189°, and *methiodide*, m. p. 260° (decomp.). The authors have little doubt that Beckett and Wright's oxynarcotine is identical with nornarceine; the substances have the same composition, $C_{22}H_{25}O_8N$, the same crystalline form, and behave alike as regards their solubility in organic solvents and in alkali hydroxides, and their insolubility in alkali carbonates.

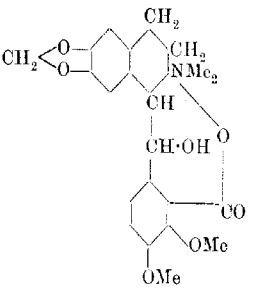
In the authors' opinion, gnoscopine is not a natural product of the plant, but is produced by racemisation of narcotine during its isolation from opium. Although the different behaviour of narcotine and gnoscopine towards acids and alkalis might well lead to the belief that they are differently constituted, there can be no doubt that the latter is *r*-narcotine (Abstr., 1910, i, 335). Since hot dilute acetic acid converts gnoscopine into cotarnine, meconine, and nornarceine (Abstr., 1907, i,

790), the changes produced by heating *l*-narcotine with dilute acetic acid are represented by the diagram :



Similar changes are effected by heating *l*-narcotine with aqueous barium hydroxide or with dilute alcohol; hot 10% sulphuric acid, however, only slowly decomposes *l*-narcotine into cotarnine and meconine, the formation of gnoscopine and nornarceine not being observed.

The behaviour of the quaternary ammonium derivatives of hydrastine and narcotine has been examined. The aqueous solution obtained by treating hydrastine methiodide (or, better, methochloride) with moist silver oxide deposits a substance, m. p. 242°, which receives, in preference to Freund's formula, the annexed constitution of an oxybetaine on account of its neutral character and inability to form a methiodide. When hydrastine methiodide or methochloride is treated with aqueous alkalis instead of with silver oxide, it is converted into methylhydrastine. Both this substance and the oxybetaine are unstable, and change into the basic keto-acid, methylhydrasteine. In the decomposition of hydrastine methiodide or of the hydroxide, no trace of meconine or of methylhydrastinine has been observed; even when the methochloride is boiled with dilute acetic acid, meconine is not formed, only the oxybetaine, m. p. 242°.



The quaternary ammonium compounds of narcotine behave in a similar manner. When the methochloride is treated with water and silver oxide, an alkaline solution is obtained, which, by keeping, deposits narceine and becomes neutral; it then contains an oxybetaine, which, however, cannot be isolated, all experiments with this object resulting in its transformation into narceine. When narcotine methochloride is treated with aqueous sodium hydroxide, it is converted into methylnarcotine (*methiodide*, $C_{23}H_{25}O_7N,MeI$, m. p. about 260°), which is changed by methyl iodide and methyl alcohol into the methiodide of narceine methyl ester by addition of methyl iodide, opening of the lactone ring, and addition of methyl alcohol. Methylnarcotine is converted with great ease, even by boiling water, into the basic keto-acid, narceine.

An important result of the preceding experiments is the following. Hydrastine and narcotine and their derivatives, containing tervalent nitrogen, experience a rupture of the carbon chain by hydrolytic decomposition, and yield meconine, cotarnine, etc. Derivatives containing quinquevalent nitrogen, however, retain the carbon chain

unbroken, but yield basic keto-acids by opening of the *iso*quinoline ring. C. S.

Vegetable Betaines and Stachydrine. ERNST SCHULZE and G. TRIER (*Zeitsch. physiol. Chem.*, 1910, **69**, 326—328. Compare Abstr., 1909, i, 323).—A reply to Engeland. Purely polemical. J. J. S.

Conversion of Hydroxymethyleneacetophenone into Benzoylpyruvic Acid and Some New Derivatives. OTTO MUMM and GEORG MÜNCHMEYER (*Ber.*, 1910, **43**, 3335—3345).—The imino-chlorides of aromatic acid-anilides undergo displacement of the halogen by the cyano-group by treatment with aqueous potassium cyanide, and react with the sodium salts of organic acids to form diacylanilides (Abstr., 1910, i, 311). The formation of diacylamines from the methiodides of 5-alkyl*iso*oxazoles and the sodium salts of organic acids is probably due to the intermediate change of the *iso*oxazole to an imino-iodide, thus:

$$\begin{matrix} CPh{-}O \\ \| \\ CH{\cdot}CH \end{matrix}\!\!>\!N,MeI \longrightarrow CH_2Bz{\cdot}CI{:}NMe,$$

which is then converted into the diacylamine, $CH_2Bz{\cdot}CO{\cdot}NMeX$ (X = acyl). If this is so, the methiodides of 5-alkyl*iso*oxazoles should react with potassium cyanide in accordance with the equation $\begin{matrix} CPh{-}O \\ \| \\ CH{\cdot}CH \end{matrix}\!\!>\!N,MeI + KCN = KI + CH_2Bz{\cdot}C(CN){:}NMe$. This is the case (in practice, the more easily obtainable methosulphate is employed), the reaction thus furnishing a method of converting hydroxymethyleneacetophenone through the *iso*oxazole into benzoylpyruvic acid.

In Claisen's method of preparing hydroxymethyleneacetophenone, the yield is increased by 50% by using 1½ mols. of ethyl formate instead of 1 mol. 5-Phenyl*iso*oxazole, obtained from hydroxymethyleneacetophenone by Zöpfchen's process, is treated with an equal molecular quantity of methyl sulphate, and the resulting additive compound treated with aqueous potassium cyanide in the cold, whereby *α-methylimino-β-benzoylpropionitrile*, $CH_2Bz{\cdot}C(:NMe){\cdot}CN$, m. p. 128°, yellow needles, is obtained. The nitrile is converted into ethyl benzoylpyruvate by equal parts of concentrated hydrochloric acid and alcohol, into benzoylpyruvic acid by boiling dilute hydrochloric acid, into *α-methylimino-β-benzoylpropionic acid*, $CH_2Bz{\cdot}C(:NMe){\cdot}CO_2H$, m. p. 163°, yellow needles, by cold concentrated hydrochloric acid, and into *benzoylpyruvamide*, $CH_2Bz{\cdot}CO{\cdot}CO{\cdot}NH_2$, m. p. 138° (decomp.), by cold dilute hydrochloric acid; the amide develops a dark red coloration with ferric chloride, and by treatment with sodium hydroxide or sodium carbonate forms a *sodium* derivative which decomposes after a long time, yielding acetophenone. With a methyl-alcoholic solution of sodium methoxide or potassium hydroxide, the nitrile yields methyl methyliminobenzoylacetate. C. S.

2:3-Diketo-5-phenylpyrroline, a Uninuclear Analogue of Isatin. OTTO MUMM and GEORG MÜNCHMEYER (*Ber.*, 1910, **43**, 3345—3359).—By passing hydrogen chloride into a well-cooled paste

of α-methylimino-β-benzoylpropionitrile (preceding abstract) in methyl alcohol, a dark red substance, *2-keto-3-methylimino-5-phenylpyrroline hydrochloride*, $\begin{matrix}CPh{:}CH\\ |\\ NH{\cdot}CO\end{matrix}\!\!>\!C{:}NMe,HCl$ (see below for constitution), is obtained, which crystallises with $2H_2O$ (m. p. about 114°) or with H_2O (m. p. 147—150°), according to the method of isolation; the *picrate*, $C_{17}H_{13}O_8N_5$, m. p. 178°, is anhydrous. By treatment with cold water it is converted quantitatively into methylamine hydrochloride and *2 : 3-diketo-5-phenylpyrroline*, $NH\!<\!\begin{matrix}CO{-}CO\\ |\\ CPh{:}CH\end{matrix}$, m. p. 216°, which crystallises in brick-red leaflets. The proof that these two substances are cyclic compounds, not derivatives of benzoylpyruvic acid, rests on their colour, the absence of the ferric chloride reaction, and the analogy of the latter compound to isatin. The formation of the former is explained by the intermediate production of an imino-ether, $CH_2Bz{\cdot}C(:NMe){\cdot}C(:NH){\cdot}OMe$, since the substance is only produced in alcoholic solution. 2 : 3-Diketo-5-phenylpyrroline forms an *oxime*, yellow plates, decomp. 213° (from which a *dioxime*, m. p. 181—182°, can be obtained, the absence of colour of which renders it doubtful whether the compound has a cyclic structure), a *phenylhydrazone*, yellowish-red needles, m. p. 240° (decomp.), and a *p-nitrophenylhydrazone*, dark red needles, m. p. about 285° (decomp.); the production of the same three substances from 2-keto-3-methylimino-5-phenylpyrroline hydrochloride determines the presence of the oximino-group in position 3. Diketophenylpyrroline forms colourless solutions in aqueous sulphurous acid or sodium hydrogen sulphite; an impure additive compound can be isolated in the latter case. Diketophenylpyrroline shows its analogy to isatin, not only by responding to the indophenin reaction, but also by its behaviour with cold sodium hydroxide, whereby a bluish-violet solution is obtained, the colour of which disappears after a few minutes, and, after acidification, *γ-iminobenzoylpyruvic acid*, $NH{:}CPh{\cdot}CH_2{\cdot}CO{\cdot}CO_2H$, m. p. 161°, is formed, which differs from the isomeric benzoylpyruvamide (*loc. cit.*) in forming a stable *sodium* salt, and in developing an orange-red coloration with ferric chloride. *γ-Iminobenzoylpyruvamide*, $NH{:}CPh{\cdot}CH_2{\cdot}CO{\cdot}CO{\cdot}NH_2$, m. p. 158—159°, is obtained by treating diketophenylpyrroline with concentrated ammonia at the ordinary temperature; it has neither acidic nor basic properties, develops an orange-red coloration with ferric chloride, and, like the γ-imino-acid itself, is converted into benzoylpyruvic acid by evaporating its solution in 50% alcohol containing a little hydrochloric acid.

By treatment with cold aqueous sodium hydrogen carbonate, 2-keto-3-methylimino-5-phenylpyrroline hydrochloride is converted into a *hydroxide*, m. p. 110—120°, which, on account of its faint greenish-yellow colour and feebly basic character, receives the constitution of a ψ-base, $NHMe{\cdot}C(OH)\!<\!\begin{matrix}CH{:}CPh\\ |\\ CO{-}NH\end{matrix}$; it is characterised by forming equally intensely coloured salts with either sodium hydroxide or with hydrochloric acid. These salts are therefore constituted alike; the

sodium salt receives the constitution $NMe{:}C\begin{cases}CH{=}{=}CPh\\ C(ONa){:}N\end{cases}$, the hydrochloride that given above. C. S.

Action of Pyridine on Iridiodisulphates. MARCEL DELÉPINE (*Compt. rend.*, 1910, **151**, 878—880. Compare Abstr., 1909, ii, 408).—A solution of ammonium iridiodisulphate does not lose its green colour when mixed with pyridine, but a change takes place, especially on boiling the liquid. The solution then contains *pyridinoiridiodisulphuric acid*, $OHIr(C_5H_5N)(SO_4H)_2$, and gives crystalline precipitates with salts of sodium, potassium, rubidium, cæsium, thallium, silver, strontium, barium, lead, and chromium. Salts have been analysed having the following formulæ, in which R represents the group $[OH{\cdot}(C_5H_5N)Ir(SO_4)_2]''$:—$R(NH_4)_{1\cdot5}5H_2O$, $RNa_{4\cdot3}H_{2\cdot3},1{\cdot}5H_2O$, $RK_{4\cdot3}H_{2\cdot3},2H_2O$, $RBa_{2\cdot3}H_{2\cdot3},3H_2O$, $RAg_{4\cdot3}H_{2\cdot3},H_2O$. The salts are deep green and form olive-green solutions. The barium salt is very sparingly soluble, and owing to its crystalline form can be used to characterise the acid or its salts. W. O. W.

[**Constitution of Benzoylanthranil.**] GUSTAV HELLER (*Ber.*, 1910, **43**, 3365).—Mumm and Hesse regard the constitution, $C_6H_4\begin{cases}N{:}CPh\\ CO{\cdot}O\end{cases}$, of benzoylanthranil as being definitely proved by the formation of benzoylanthranil and aniline by the interaction of anthranilic acid and benzanilideiminochloride (Abstr., 1910, i, 770). The author fails to see why the reaction cannot be explained by the following scheme, which leads to the constitution of benzoylanthranil proved by his own experiments: $CO_2H{\cdot}C_6H_4{\cdot}NH_2 + CClPh{:}NPh \longrightarrow C_6H_4\begin{cases}NH{\cdot}CPh{:}NPh\\ CO_2H\end{cases} \longrightarrow C_6H_4\begin{cases}N{\cdot}COPh\\ CO\end{cases} + NH_2Ph$. C. S.

Quinoline-5-carboxylic Acid. I. ZYG. VON JAKUBOWSKI (*Ber.*, 1910, **43**, 3026—3032. Compare Abstr., 1909, i, 264).—To prepare quinoline-5-carboxylic acid, *o*-amino-*p*-tolunitrile is condensed with glycerol in presence of arsenic acid to 5-methylquinolyl-8-carboxylic acid. On distillation with calcium hydroxide, 5-methylquinoline is obtained, and this is oxidised to the 5-carboxylic acid, which is similar to the ψ-quinoline-*ana*-carboxylic acid described by Lellmann and Alt (compare Abstr., 1887, 502, 737, 973; 1888, 296, 499).

5-Methylquinoline-8-carboxylic acid, $C_9NH_6Me{\cdot}CO_2H$, crystallises in small needles of silvery lustre, m. p. 173—174°. The *ammonium*, *calcium*, and *copper* salts are described: the *hydrochloride* forms concentrically grouped needles; the *nitrate*, long needles of silky lustre; the *picrate*, slender, yellow needles, m. p. 205—207°; the *platinichloride*, pale yellow, concentrically intergrown needles, and the *dichromate*, orange rods.

By the distillation of 5-methylquinoline-8-carboxylic acid with calcium oxide, a by-product is formed, which crystallises in colourless needles, m. p. 200—202°. This is probably a new dimethyldiquinonyl; it is not identical with 5 : 5′-dimethyl-8 : 8′-diquinonyl. The main product

is 5-*methylquinoline*, a colourless liquid, b. p. 253—255°/735 mm. The *picrate* forms light yellow plates, which soften at 200°, m. p. 210—213°. The *mercurichloride* forms small, colourless needles; the *platinichloride*, bright orange needles; the *methiodide*, yellow, silky needles, m. p. 105°.

On oxidation with a mixture of chromic and sulphuric acids, quinoline-5-carboxylic acid is obtained. E. F. A.

Aromatic Hydrazines. VIII. Oxidation of Diphenylhydrazine. HEINRICH WIELAND and ERNST WECKER (*Ber.*, 1910, 43, 3260—3271).—The reddish-violet dye prepared by the action of acid oxidising agents, more particularly of hypochlorous acid, on diphenylhydrazine (compare E. Fischer, Abstr., 1878, 313) is the hydrochloride of quinoneanildiphenylhydrazone,

$$NPh{:}C_6H_4{:}N{\cdot}NPh_2,HCl.$$

This constitution follows from: (*a*) analysis; (*b*) the products of reduction, namely, diphenylamine and *p*-aminodiphenylamine; (*c*) its oxidation value as determined by Willstätter and Piccard's method (*Ber.*, 1908, **41**, 1474). Attempts to synthesise the dye by the condensation of quinoneanil with diphenylhydrazine hydrochloride showed that the chief products were tetraphenyltetrazen and *p*-hydroxydiphenyl, together with a brilliant bluish-violet dye, which on reduction gave diphenylamine and an unknown *p*-hydroxyaminodiphenylamine. In the formation of this bluish-violet dye, an additive product is probably formed, which is oxidised by the excess of quinoneanil to an ortho-quinonoid compound, $NPh_2{\cdot}N{:}C\begin{cases}C(:NPh)—CH\\ \|\quad\quad\|\\ CH{:}C(OH){\cdot}CH\end{cases}$, the hydrochloride of which is the dye.

It is shown that in the formation of the red dye, diphenylhydroxylamine is probably an intermediate product, which condenses with the diphenylhydrazine, yielding the triazo-derivative, $NH(NPh_2)_2$. This then undergoes a type of molecular rearrangement resembling that of diazoamino-compounds, thus yielding $NHPh{\cdot}C_6H_4{\cdot}NH{\cdot}NPh_2$, which is oxidised to the dye base, $NPh{:}C_6H_4{:}N{\cdot}NPh_2$. Further confirmation of this view is afforded by the fact that tetraphenylhydrazine, which is known to be readily hydrolysed to diphenylamine and diphenylhydroxylamine (Wieland, Abstr., 1907, i, 1076; 1908, i, 1014), reacts with a glacial acetic acid solution of diphenylhydrazine at 55—60°, yielding the red dye. Di-*p*-tolylhydrazine does not yield a dye when oxidised, but when warmed with glacial acetic acid and tetraphenylhydrazine gives a red dye. The formation of a dye cannot therefore be merely due to the oxidising action of the tetraphenylhydrazine on the diphenyl or di-*p*-tolylhydrazine, but must be due to the hydrolysis to diphenylhydroxylamine, which then condenses with the secondary hydrazine.

p-Substituted tetraphenylhydrazines do not yield dyes with di-*p*-tolylhydrazine.

Quinoneanildiphenylhydrazone hydrochloride, $C_{24}H_{19}N_3HCl$, is deposited in glistening, bronzy-green crystals, m. p. 147°, when light petroleum is added to its alcoholic ethereal solution. The yield is poor, and the method of purification is tedious. Both the solid and its

solutions are stable. It dyes cotton mordanted with tannin a brilliant violet-red. Its solution in concentrated sulphuric acid has a greenish-blue colour, but turns reddish-violet when diluted. When boiled for some time with mineral acids, it yields small amounts of diphenylamine, and when shaken with 20% sulphuric acid and lead peroxide yields quinone. The *base* has only been obtained in the form of an amorphous, reddish-brown powder. The majority of its salts and double salts are sparingly soluble in water, and do not crystallise well. Solutions do not give any characteristic absorption bands.

p-Methyl- and *p*-methoxy-diphenylhydrazine give similar dyes, but the di-*p*-tolyl and dianisyl compounds do not.

p-Hydroxy-o-quinoneanildiphenylhydrazone hydrochloride, $C_{24}H_{19}ON_3,HCl$, obtained by condensing quinoneanil with diphenylhydrazine hydrochloride, is more soluble in water than the red dye, and the solutions have more of a bluish tint. The *base* has a fiery brownish-red colour, and is amphoteric; it dissolves in both acids and alkalis, giving brilliant violet solutions. When reduced with stannous chloride, it yields *p-hydroxy-o-aminodiphenylamine*, $NHPh\cdot C_6H_3(OH)\cdot NH_2$, which crystallises from alcohol, has m. p. 170—171°, and dissolves in both acids and alkalis.

These solutions are readily oxidised to blue amphoteric dyes.

J. J. S.

Phenylhydrazones of Dextrose. Robert Behrend and Willy Reissberg (*Annalen*, 1910, 377, 189—220).—The phenylhydrazone of dextrose, like dextrose itself, exists in two forms, which exhibit birotation, and, when dissolved, give ultimately identical solutions by the formation of the same equilibrium mixture. The theory advanced by Behrend and Lohr (Abstr., 1908, i, 765) that one of these dextrose-phenylhydrazones is a true hydrazone,

$$CH_2(OH)\cdot[CH(OH)]_4\cdot CH{:}N\cdot NHPh,$$

and the other a hydrazide,

$$CH_2(OH)\cdot CH(OH)\cdot \overset{\displaystyle |\!\!-\!\!-O\!\!-\!\!-|}{CH}\cdot[CH(OH)]_2\cdot CH\cdot NH\cdot NHPh,$$

has been proved in the following ways.

By treatment with acetic anhydride in pyridine, dextrose-β-phenylhydrazone yields an amorphous acetate, whilst dextrose-α-phenylhydrazone gives a crystalline acetate, m. p. 152—153°, together with an amorphous acetate (Hofmann, Abstr., 1909, i, 519). (The author shows that these are penta-acetates, and that the last-mentioned, amorphous acetate is a mixture of the other two.) True hydrazones yield *N*-acetyl derivatives only with difficulty, and are not attacked by acetic anhydride in cold pyridine. Since the crystalline dextrose-α-phenylhydrazone penta-acetate, by treatment with aqueous-alcoholic potassium hydroxide and benzaldehyde, yields acetylphenylbenzylidenehydrazine, whilst the amorphous dextrose-β-phenylhydrazone penta-acetate under similar conditions gives phenylbenzylidenehydrazine, it follows that dextrose-α-phenylhydrazone penta-acetate contains an acetyl group attached to a nitrogen atom and is therefore produced from a hydrazide, and that dextrose-β-phenylhydrazone penta-acetate

does not contain an acetylated nitrogen atom and is therefore produced from a true hydrazone. Dextrose-α-phenylhydrazone and dextrose β-phenylhydrazone have the hydrazide and the hydrazone constitution respectively. This conclusion is supported by the fact that dextrose-α-phenylhydrazone penta-acetate yields α-acetylphenylhydrazine by hydrolysis with 5% hydrochloric acid, whilst the β-isomeride resinifies.

Another proof of the theory is furnished by condensing dextrose with α-acetylphenylhydrazine in warm alcohol containing a little acetic acid. The condensation product is a syrup from which a crystalline substance cannot be isolated, but from which, after treatment with acetic anhydride in cold pyridine, dextrose-α-phenylhydrazone penta-acetate has been obtained; this acetate, therefore, certainly has an acetyl group attached to a nitrogen atom. If the original syrupy condensation product contains a true hydrazone, there must still be five hydroxyl groups in its dextrose nucleus capable of acetylation. The fact that the product obtained by acetylating the syrup in pyridine contains, in addition to dextrose-α-phenylhydrazone penta-acetate, a *hexa-acetate*, shows that a true hydrazone must be present in the syrupy mixture of the dextroseacetylphenylhydrazines. This hexa-acetate, $C_{24}H_{30}O_{11}N_2$, which is separated from the accompanying penta-acetate by solution in ether, is an amorphous powder having $[\alpha]_D + 143{\cdot}1°$ in pyridine and 137·9° in benzene without mutarotation.

Dextrose-α-phenylhydrazone penta-acetate, obtained by Hofmann's method (*loc. cit.*), has m. p. 152—153°, and $[\alpha]_D + 11{\cdot}97°$ in pyridine.

The acetate separated by ether from the crude acetylated product partly melts at 130°, resolidifies, and then has m. p. 150—152°; if after being heated to 150° the acetate is recrystallised from alcohol, it has m. p. 152° without previous fusion at 130°. When the crude acetylated product is treated with an amount of ether insufficient for complete solution, the residual sparingly soluble substance has m. p. 110°, then resolidifies, and changes into the acetate, m. p. 152—153°. The latter can be converted into the substance having m. p. 110° by gently boiling its solution in ether. In pyridine the two substances have the same specific rotation, $[\alpha]_D + 17{\cdot}5°$, without mutarotation. The relation between the two substances is not yet settled; it appears to be due to polymorphism.

α-Acetylphenylhydrazine can be obtained in 76·84% yield by hydrolysing β-formyl-α-acetylphenylhydrazine with concentrated hydrochloric acid; when the hydrolysis is effected by aqueous potassium hydroxide, β-formylphenylhydrazine is produced. C. S.

1-Benzoylphenyl-3-methyl-5-pyrazolone. HENRY A. TORREY and H. R. RAFSKY (*J. Amer. Chem. Soc.*, 1910, **32**, 11, 1489—1492).—The pyrazolone was prepared by Michael's method from the hydrochloride of *p*-hydrazinobenzophenone and acetoacetic acid. Modifications were introduced in the preparation of *p*-aminobenzophenone (Döbner, *Annalen*, 1881, **210**, 267) and of *p*-hydrazinobenzophenone (Ruhemann and Blackman, Trans., 1889, i, 613).

1-*Benzoylphenyl*-3-*methyl*-5-*pyrazolone*, $\begin{matrix}CH_2\cdot CO\\ |\\ CMe{=}N\end{matrix}\!\!>\!N\cdot C_6H_4Bz$, forms

brownish-yellow crystals, m. p. 170—171°. It gives a white, flocculent precipitate with silver nitrate, and does not reduce Fehling's solution. Its *hydrochloride* was obtained as a pale brown powder, m. p. 196° (decomp.), turning dark at 180°. A small amount of *1-benzoylphenyl-2:3-dimethyl-5-pyrazolone* was obtained, m. p. 125°. N. C.

Oxidoanhydro-compounds. I. STEFAN VON NIEMENTOWSKI (*Ber.*, 1910, **43**, 3012—3026).—The two first members of the series of oxyanhydro-compounds, namely, benziminazole oxide and 2-methylbenziminazole oxide, were hitherto unknown; they have now been obtained by reduction of *o*-nitroformanilide and *o*-nitroacetanilide with ammonium sulphide in alcoholic solution.

Benziminazole oxide, when treated with benzoyl chloride and sodium hydroxide, undergoes intramolecular rearrangement to *o*-phenylenecarbamide, $C_6H_4<^{NH}_{NH}>CO$, m. p. 310°. The same rearrangement is observed on heating with hydrochloric acid in sealed tubes at 200°, on fusion with potassium hydroxide, and on heating with zinc dust at 230°. Apparently, the carbamide is the stable isomeride; it has not been found possible to convert it into oxidobenziminazole.

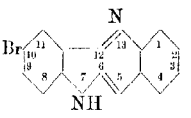
o-Nitroformanilide is prepared by heating *o*-nitroaniline with anhydrous formic acid. The reduction product, *benziminazole oxide*, $O<^{N=C_6H_4}_{CH\cdot NH}$, forms colourless needles, m. p. 210°, to a colourless liquid, decomp. 212°. It gives a reddish-yellow coloration with ferric chloride. The *hydrochloride* forms slender needles, m. p. 200—214°; the *aurichloride* forms golden-yellow, prismatic needles in tree-like aggregates, m. p. 172°; the *platinichloride* separates in stout, bright orange rods, decomp. 220°.

2-Methylbenziminazole oxide, $O<^{N=C_6H_4}_{CMe\cdot NH}$, forms snow-white needles, m. p. 251°. The *hydrochloride* forms colourless needles; the *aurichloride* separates in golden-yellow, broad rods, m. p. 175° (decomp.); the *platinichloride*, in lustrous, yellow columns, m. p. 245°; the *sulphate* forms colourless needles or transparent plates, m. p. 174°. Those reagents which convert the lower homologue into phenylenecarbamide are without action. E. F. A.

Some Derivatives of Quindoline. FRITZ FICHTER and FRANZ ROHNER (*Ber.*, 1910, **43**, 3489—3499. Compare Fichter and Boehringer, Abstr., 1907, i, 92).—Quindoline is obtained in 75—80% yield by boiling the sodium salt of flavindine (quindoline-carboxylic acid) with 10% potassium hydroxide and zinc dust until the solution is colourless, filtering rapidly, and passing air through the filtrate, whereby quindoline is precipitated.

The reaction between quindoline and bromine in cold glacial acetic acid yields an unstable, dark yellow *bromo-perbromide*, $C_{15}H_{10}N_2Br_8$, which is converted by crystallisation from alcohol into *10-bromoquindolinium bromide*, $C_{15}H_{10}N_2Br_2$, yellow needles; this substance, which contains

one ionisable bromine atom, is converted by alcoholic potassium hydroxide into 10-*bromoquindoline*, (annexed constitution), m. p. 304°, pale yellow needles. The position of the halogen atom is determined only by the fact that bromine first attacks the indole imino-group and then wanders to the para-position. The attack of bromine at position 7 is rendered probable by the fact that substitution does not occur when 7-acetylquindoline and bromine react in glacial acetic acid; a dark red, unstable perbromide is obtained, which is converted by crystallisation into 7-*acetylquindolinium bromide*, $C_{17}H_{12}ON_2,HBr$, m. p. 272°, yellow needles, from which quindoline is produced by the action of alkalis.



A concentrated solution of quindoline in glacial acetic acid reacts with solid sodium nitrite, in the cold forming pale yellow needles of *quindolinium nitrite*, $C_{15}H_{10}N_2,HNO_2$, when heated yielding 7-*nitrosoquindoline*, m. p. 275°, dark red needles, which forms a blue solution in strong, alcoholic potassium hydroxide, and yields quindoline by hydrolysis with alcoholic hydrogen chloride. By reduction with tin and hydrochloric acid, quindoline is converted into 5:13-*dihydroquindoline*, m. p. 172° (rapidly heated), which is oxidised very easily, even by atmospheric oxygen, to quindoline. On treatment with acetic anhydride in the cold, dihydroquindoline yields 13-*acetyl*-5:13-*dihydroquindoline*, m. p. 162°, a monoacidic base, which oxidises less readily than dihydroquindoline. When boiled with acetic anhydride, dihydroquindoline is converted into 7:13-*diacetyl*-5:13-*dihydroquindoline*, m. p. 235°. Acetyldihydroquindoline and an excess of bromine in glacial acetic acid yield a yellow *perbromide*, from which 5:10-*dibromo*-13-*acetyl*-5:13-*dihydroquindoline*, m. p. 242°, is readily obtained. This substance suffers hydrolysis and oxidation when boiled with 40% sulphuric acid, yielding 5:10-*dibromoquindoline*, m. p. 221°, yellow needles.

13-*Methyl*-5:13-*dihydroquindolinium iodide*, $C_{16}H_{14}N_2HI$, is obtained by the methylation of dihydroquindoline or by the reduction of 13-methylquindolinium iodide by tin and hydrochloric acid, during which the *stannochloride*, $C_{16}H_{14}N_2,2HCl,SnCl_2$, is obtained. 13-*Methyl*-5:13-*dihydroquindolinium perchlorate*, $C_{16}H_{14}N_2,HClO_4$, obtained from an alcoholic solution of the iodide and perchloric acid, crystallises in golden leaflets. The base corresponding with these salts is so unstable that it changes in air into 13-methylquindolinium carbonate (*loc. cit.*).

C. S.

Pechmann's Isomeric Hydrazidines. MAX BUSCH and RICHARD RUPPENTHAL (*Ber.*, 1910, 43, 3001—3011).—Pechmann (Abstr., 1896, i, 32) has described two forms, m. p. 119° and 174° respectively, of diphenylbenzenylhydrazidine, to which he assigned the formulæ NHPh·CPh:N·NHPh and NPh:CPh·NH·NHPh, the isomerism being regarded as due to desmotropism.

It is now shown that the more fusible isomeride contains an asymmetric disubstituted hydrazine, and has the formula

$$NPh{:}CPh{\cdot}NPh{\cdot}NH_2.$$

It unites with aldehydes, forming hydrazones, and loses a nitrogen atom under the influence of nitrous acid, forming diphenylbenzenylamidine, NPh:CPh·NHPh.

The less fusible isomeride has the formula, NPh:CPh·NH·NHPh, assigned to it by Pechmann, and is converted on oxidation into the azo-compound, NPh:CPh·N:NPh.

By the interaction of benzanilide imide chloride and phenylhydrazine both isomerides are formed, the chloride attacking both the α- and β-nitrogen atoms of the hydrazine. The β-hydrazidine,

NPh:CPh·NH·NHPh,

predominates, and it was not found possible by altering the conditions to increase the proportion of the α-hydrazidine. The two isomerides are not convertible into one another. α-Diphenylbenzenylhydrazidine forms a stable *acetate*, soluble in very dilute acetic acid.

α-*Diphenylbenzylidenebenzenylhydrazidine*,

NPh:CPh·NPh·N:CHPh,

crystallises in colourless bunches of interlaced needles, which become yellow at 155°, m. p. 159—160°.

On leaving the α-diphenylbenzenylhydrazidine overnight with benzaldehyde in benzene solution, it decomposes, forming benzanilide.

Diphenyl-m-*nitrobenzylidenebenzenylhydrazidine* forms yellow needles, m. p. 173°.

The α-hydrazidine interacts with carbonyl chloride, forming a compound, $C_{20}H_{15}ON_3$, crystallising in microscopic, transparent prisms, m. p. 301—302°, which is considered to be endo*xytriphenyldihydrotriazole*, NPh<C=N / CPh—NPh>O.

Benzeneazophenyliminophenylmethane, NPh:CPh·N:NPh, crystallises in reddish-brown needles, m. p. 101—102°.

β-Diphenylbenzenylhydrazine, when boiled in alcoholic solution with benzaldehyde, forms *tetraphenyldihydrotriazole*, NPh<CHPh·NPh / CPh=N, which separates in greenish-yellow needles, m. p. 119—120°.

Similarly, the β-hydrazidine unites with formaldehyde, yielding *triphenyldihydrotriazole*, NPh<CH_2·NPh / CPh:N, which crystallises in stunted, transparent, greenish-yellow needles, softening at 120°, m. p. 124°, to a clear oil; it is faintly basic.

With carbonyl chloride, *triphenyltriazolone*, NPh<CO—NPh / CPh:N, is formed; it crystallises in colourless needles of silky lustre, m. p. 223—224°, and has neither basic nor acid properties. E. F. A.

Action of Phenylhydrazine on Ethyl Benzoylacetate. Otto Kuhling (*Ber.*, 1910, **43**, 3399).—The product previously described (Abstr., 1910, i, 780) as ketoanilinodiphenyltetrahydrotriazine can be prepared by mixing acetic acid solutions of ethyl benzoylacetate and phenylhydrazine (excess). Whether the compound has the con-

stitution originally given or whether it is the phenylhydrazide of ethyl benzoylacetate phenylhydrazone has not been determined.

J. J. S.

Synthesis of Derivatives of 1 : 2 : 7-Pyrazopyridine [1 : 2 : 7-Benztriazole]: a New Series of Homo (C·C) Condensed, Heterodicyclic Compounds. CARL BÜLOW and KARL HAAS (*Ber.*, 1910, **43**, 3401—3412).—The fact that Walther's "5-imino-1-phenyl-3-methylpyrazolone" (Abstr., 1897, i, 297) contains a labile hydrogen atom attached to the carbon atom in the α-position to the carbon to which the amino-group is attached, and condenses with solutions of benzenediazonium salts (Michaelis, Abstr., 1905, i, 478), led the authors to the conclusion that the compound would condense with β-diketones or with esters of β-ketonic acids, yielding compounds of the types: $\begin{matrix}CR{:}N\text{—}C{\cdot}NPh\\ |\quad\quad\quad\ \|\\ CH{:}CR'{\cdot}C{\cdot}CMe\end{matrix}\!\!>\!N$ and $\begin{matrix}CR{:}N\text{——}C{\cdot}NPh\\ |\quad\quad\quad\ \|\\ CH{\cdot}C(OH){\cdot}C{\cdot}CMe\end{matrix}\!\!>\!N$.

These are somewhat analogous to the hetero-condensed, heterocyclic condensation products already described (Abstr., 1909, i, 615; 1910, i, 80, 81, 203, 595), but contain a C·C-group common to the two nuclei in place of a C·N-group, and in addition the smaller ring contains a CH-group in place of a nitrogen atom. Monomethylene substituted β-ketones and β-ketonic esters react in a similar manner. The hydroxy-derivatives obtained when β-ketonic esters are used are not so strongly acetic as the heterohydroxylic acids previously described (Abstr., 1910, i, 595). As a rule, they cannot be titrated accurately by standard alkalis, using phenolphthalein as indicator, and solutions of their salts are decomposed by carbon dioxide. They form a link between the heterohydroxylic acids and the phenols proper.

1-*Phenyl*-3 : 4 : 6-*trimethyl*-1 : 2 : 7-*benztriazole*, $\begin{matrix}CMe{:}N\text{—}C{\cdot}NPh\\ |\quad\quad\quad\ \|\\ CH{:}CMe{\cdot}C{\cdot}CMe\end{matrix}\!\!>\!N$, obtained by boiling a glacial acetic acid solution of acetylacetone and 5-amino-1-phenyl-3-methylpyrazole for five hours, crystallises in large, colourless, compact, prismatic needles, m. p. 128°, and is feebly basic. The *aurichloride*, $C_{15}H_{15}N_3,HAuCl_4,H_2O$, forms long, glistening, yellow needles; the *platinichloride*, $2C_{15}H_{15}N_3,H_2PtCl_6,2H_2O$, crystallises in brown, compact, rhombic cubes, which change colour at 200°; the additive *compound* with silver nitrate forms long, colourless needles.

1-*Phenyl*-3 : 4 : 5 : 6-*tetramethyl*-1 : 2 : 7-*benztriazole*, $C_{19}H_{17}N_3$, prepared in a similar manner from methylacetylacetone, crystallises from alcohol in colourless needles, m. p. 138—139°, and 1 : 4-*diphenyl*-3 : 6-*dimethyl*-1 : 2 : 7-*benztriazole*, $C_{20}H_{17}N_3$, obtained from benzoylacetone, crystallises from 96% alcohol in slender needles, m. p. 136—137°, after sintering at 133°. It is sometimes accompanied by a by-product melting at 156—160°.

4-*Hydroxy*-1-*phenyl*-3 : 6-*dimethyl*-1 : 2 : 7-*benztriazole*, $C_{14}H_{13}ON_3$, obtained by boiling a glacial acetic acid solution of ethyl acetoacetate with the aminophenylmethylpyrazole, crystallises from hot water in glistening needles. It can be titrated by means of standard potassium

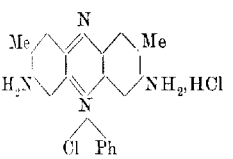
hydroxide solution, and the solution of the potassium salt gives precipitates with salts of most of the heavy metals. The *aurichloride*, $C_{14}H_{13}ON_3,HAuCl_4$, forms compact, yellow crystals, and the *platinichloride*, compact, yellowish-brown needles. The base has the properties of a feeble febrifuge. *4-Hydroxy-1-phenyl-3 : 5 : 6-trimethyl-1 : 2 : 7-benztriazole*, $C_{15}H_{15}ON_3$, obtained from ethyl methylacetoacetate, crystallises from 90% alcohol in compact, rhombic plates, m. p. 224—226°; the *aurichloride* forms stout, yellow rods. *4-Hydroxy-1-phenyl-3 : 6-dimethyl-4-ethyl-1 : 2 : 7-benztriazole*, $C_{10}H_{17}ON_3$, sinters at 181°, and has m. p. 183—184°.

The dissociation constant of 7-hydroxy-5-methyl-1 : 2 : 4 : 9-benztetrazole (Abstr., 1910, i, 595) is practically the same as that of valeric acid. J. J. S.

Synthesis of Safranines. III. N. N. Orloff (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 939—949. Compare Abstr., 1910, i, 782—783).—The safranines can be readily obtained by the condensation of *p*-benzoquinonedichlorodi-imide or its homologues and analogues with 4-phenyltolylene-2 : 4-diamine or its homologues and analogues, the best yields being obtained with one molecule of the former to two of the latter. The safranines of various constitutions (containing benzene, toluene, or naphthalene nuclei) all have similar physical properties, their red colour becoming bluish as the molecular weight increases.

Aminoazotoluene, on reduction and subsequent treatmont with bleaching powder, yields *p-toluquinonedichlorodi-imide*, $C_7H_6N_2Cl_2$, m. p. 74°, decomposes at 155°, and forms long, yellow, needle-shaped crystals.

3 : 7-Diamino-5-phenyl-2 : 8-dimethylphenazonium chloride, to which the annexed formula, namely, that of ordinary tolusafranine, is assigned, obtained by the condensation of *p*-toluquinonedichlorodi-imide with 4-phenyltolylene-2 : 4-diamine, forms bright yellowish-green crystals. Alkali hydroxides precipitate the free *base* from ethereal solutions of the hydrochloride. The *dichromate*, $(C_{20}H_{18}N_3)_2Cr_2O_7$, was analysed. By removing one amino-group from the hydrochloride, *3-amino-5-phenyl-2 : 8-dimethylphenazonium chloride* is formed. The aqueous solution is precipitated by picric acid, tannin, and sodium acetate. Ammonia and the alkali carbonates precipitate the *base*, of which the *dichromate*, $(C_{20}H_{18}N_3)_2Cr_2O_7$, was analysed.



The *acetyl* derivative of aminotolusafranine when treated with ammonia yields tolusafranine. When the second amino-group is removed from the monoamine, the chromogen, *5-phenyl-2 : 8-dimethylphenazonium*, is obtained in the form of its ferric chloride compound,

$$C_{20}H_{17}N_2FeCl_4.$$

It forms brown crystals, m. p. 190°, which, when treated with ammonia and then with hydrochloric acid, yields dimethyl*apo*safranine hydrochloride, which is identical in all respects with the monoaminophenazonium from which the chromogen was obtained. Z. K.

Quinonoid Compounds. XXIV. Aniline-black. IV. Richard Willstätter and Carl Cramer (*Ber.*, 1910, **43**, 2976—2988. Compare Abstr., 1909, i, 535, 975).—Aniline-black is regarded as containing eight para-substituted benzene nuclei. The two stages of oxidation product contains three and four quinonoid nuclei respectively. A quantitative determination of these has been made by reduction with phenylhydrazine carbamate in an atmosphere of carbon dioxide and measurement of the nitrogen liberated. Reduction takes place in sharply differentiated stages, according to the temperature. In the case of dichromate black, one molecule of hydrogen is introduced at 30—35°, the colour changing to light blue; at 75—80° the colour becomes grey, and a further reduction takes place; lastly, between 120° and 150°, the colourless leuco-base is formed. The hydrolysed blacks are more stable; thus hydrolysed dichromate black is stable until 80°, loses a second quinonoid nucleus at 130—150°, and can only be completely reduced on the addition of a trace of Green's black, which acts as a catalyst. Chlorate-black contains four quinonoid nuclei; the first is attacked at 35—40°, the second at 80—110°, and the remaining two at 120—150°, the colour changing from dark violet through dull blue and brown to a light brownish-grey. Hydrolysed chlorate-black retains two nuclei at 150°, but parts with these in presence of Green's black.

Green's black, obtained on oxidising aniline salts with atmospheric oxygen in presence of copper sulphate and phenylenediamine, is very readily reduced, all four nuclei being attacked below 110°. When hydrolysed Green's black loses the quinonoid nuclei in turn at 80—100°, 115—130°, 130—140°, 140—150°. The behaviour of Green's black is attributed to the catalytic action of traces of impurity. The apparatus used is described and experimental data given of its testing with seven quinonoid compounds. E. F. A.

History of Diazohydrazides. Emil Fischer (*Ber.*, 1910, 43, 3500—3501).—Dimroth and de Montmollin (Abstr., 1910, i, 898), in their account of the diazohydrazides, omit to mention that the first member of this class to be discovered was diazobenzene-ethylhydrazide, obtained by the author from diazobenzene chloride and ethylhydrazine in aqueous solution (*Annalen*, 1879, **199**, 306). C. S.

Biochemical Classification of the Proteins. José Rodriguez Carracido (*Anal. Fis. Quim.*, 1910, **8**, 261—263; *Revista Chim.*, 1910, **6**, 314—315).—A scheme for the classification of the proteins founded more on biochemical than on chemical considerations. W. A. D.

General Protein Chemistry. III. The Denaturation of Serum Albumin. Léonor Michaelis and Peter Rona (*Biochem. Zeitsch.*, 1910, **29**, 494—500).—If serum albumin is changed by heating, and then caused to coagulate by bringing the mixture to the isoelectric point, two stages in the denaturation can be detected. If the heating is not too long continued, the protein is obtained in the first stage of change, in which by the action of hydrochloric acid, it is rendered soluble and converted apparently in the original protein.

If the heating be continued for a longer time, the second stage is reached in which the coagulum is soluble in acid only with difficulty, and in which the reaction is irreversible. S. B. S.

The Fractional Precipitation of the Milk Proteins. ALBERT J. J. VANDERVELDE (*Biochem. Zeitsch.*, 1910, 29, 461—464).—As protein-α is described, that protein which is precipitated on the addition of acid, and as protein-β, that which separates from the filtrate from protein-α on coagulation. The author has estimated the amounts of these proteins in the whole milk, and in the fractions obtained by the additions of varying quantities of acetone, ethyl and methyl alcohols to the milk. From the results obtained, which are tabulated, the author draws the conclusion that it is not possible to conclude that milk caseinogen and milk albumin have distinct individuality. S. B. S.

Combination of Lactic Acid and Casein. W. VAN DAM (*Chem. Weekblad*, 1910, 7, 1013—1019).—By means of Bredig's ethyl diazoacetate method, the author has determined the reduction in the concentration of the hydrogen ions in solutions of lactic acid produced by addition of increasing amounts of casein. In solutions containing a large excess of hydrogen ions, the casein combines with a constant amount of lactic acid, 4·25%. Assuming that 1 molecule of lactic acid combines with 1 molecule of casein, the molecular weight of the protein is 2118. On the assumption that 1 molecule of potassium hydroxide neutralises 1 molecule of casein, Robertson (Abstr., 1910, ii, 679) gives 556 as the molecular weight. It follows that one basic group is present for every four replaceable hydrogen atoms in the casein molecule. A. J. W.

Electrochemistry of Proteins. III. Dissociation of Salts of Ovimucoid in Solutions of Varying Alkalinity and Acidity. T. BRAILSFORD ROBERTSON (*J. Physical Chem.*, 1910, **14**, 709—718. Compare Abstr., 1910, ii, 679).—Mörner's ovimucoid, that part of the white of egg proteins which is not precipitated by boiling dilute acetic acid, but is precipitated by concentrated alcohol (Abstr., 1894, i, 264), was obtained as a dry white powder. It has been investigated by the method previously used with caseinogen.

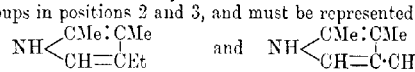
Unlike caseinogen and globulin, ovimucoid dissolves readily, and is more basic than acidic. One gram requires $7{\cdot}0 \times 10^{-5}$ gram-equivalents of hydrogen chloride to produce a solution which is neutral to litmus, and solutions containing less acid are alkaline. In very dilute potassium hydroxide solutions, ovimucoid tends to combine with the whole of the alkali, but the proportion of potassium hydroxide combined decreases with concentration, until in strongly alkaline solution the ovimucoid attains a maximum combining capacity of 50×10^{-5} gram-equivalents of alkali per gram.

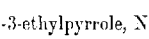
The combining capacity for acid also increases, and tends to attain a constant value in presence of large excess of acid. The constant was never attained, but is probably greater than 100×10^{-5} gram-equivalents of acid per gram. The addition of ovimucoid to alkali or

acid of concentration less than $N/10{,}000$ increases the conductivity by reason of the considerable conductivity of the free protein. The conductivity of stronger solutions is considerably diminished by the protein. The depression in conductivity, λ, brought about by addition of 1% of ovimucoid to solutions of potassium hydroxide at 36° is expressed by $\lambda = 0{\cdot}2085b - 12{\cdot}5b^2 - 0{\cdot}000356$, and in the case of hydrogen chloride by $\lambda = 0{\cdot}4199a - 8{\cdot}527a^2 - 0{\cdot}000414$, where b and a are the concentrations of alkali and acid respectively. A similar expression was deduced in the case of caseinogen, in which, however, the factor c, the concentration of the protein, was introduced.

The author endeavours to trace a theoretical connexion between the constants 0·2085 and 0·4199 in the above equations, and the values 0·218 and 0·384 of the conductivities of potassium hydroxide and hydrogen chloride respectively at infinite dilution. R. J. C.

The Constitution of the Coloured Constituent of the Pigment of Blood. Oskar Piloty [with Eugen Quitmann and Paul Eppinger] (*Annalen*, 1910, **377**, 314—369. Compare Abstr., 1909, i, 539).—The acid previously termed hæmopyrrolecarboxylic acid is not derived from hæmopyrrole, but from an isomeride, and hence the name *phonopyrrolecarboxylic acid* is suggested; by the elimination of carbon dioxide from this acid, a dimethylethylpyrrole (*phonopyrrole*) is obtained, which is not identical with hæmopyrrole. Both compounds must be represented as dimethylethylpyrroles with a methyl group in position 2, and methyl and ethyl groups in positions 3 and 4 or 4 and 3. As phonopyrrolecarboxylic acid shows no tendency to yield an indole derivative, it is improbable that the methyl and $\cdot CH_2 \cdot CH_2 \cdot CO_2H$-groups are in the relative positions 2 and 3. This conclusion is confirmed by the fact that hæmatopyrrolidinic acid (Abstr., 1909, i, 540), which is formed by the union of molecular quantities of phonopyrrolecarboxylic acid and hæmopyrrole, on decomposition loses propionic acid from the phonopyrrolecarboxylic acid portion of the molecule, and yields 2 : 3-dimethylpyrrole. Phonopyrrole and its carboxylic acid must therefore have the two methyl groups in positions 2 and 3, and must be represented by the formulæ:



and hæmopyrrole as 2 : 4-dimethyl-3-ethylpyrrole, 

An ethereal solution of phonopyrrolecarboxylic acid reacts with a 0·2*N*-solution of benzenediazonium chloride, yielding a dark red *azo-dye*, $C_{15}H_{18}O_2N_3Cl$, m. p. 145—146° (decomp.). Phonopyrrolecarboxylic acid is scarcely affected when fused with potassium hydroxide at 300° for half an hour, or when distilled under very low pressures, but at atmospheric pressure it loses carbon dioxide at 250—330°, and gives a 28% yield of *phonopyrrole*, which is best purified by steam distillation. After distillation over barium oxide it has b. p. 96—98°/19 mm., and is readily distinguished from the isomeric hæmopyrrole, as it yields an oily *picrate*, which does not solidify when placed in a freezing mixture, and reacts with nitrous acid, yielding

a small amount of a syrupy maleinimide derivative (compare Abstr., 1910, i, 133).

Full details for the reduction of hæmatoporphyrin with tin and hydrochloric acid are given, and also for the preparation of hæmatopyrrolidinic acid free from tin. The acid is soluble in water to an appreciable extent, but yields precipitates with many salts and alkalis; these precipitates appear to be adsorption products. Hæmopyrrole forms an unstable compound with the acid. When the zinc derivative of the acid is fused with potassium hydroxide (compare Abstr., 1910, i, 857), water and the loosely-combined hæmopyrrole are evolved at 170—200°; at 270° a dark oil is formed, and the temperature is kept at 270° by dropping water gradually into the retort, but towards the end the temperature is raised to 320°.

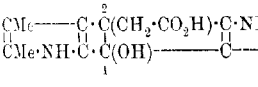
The products isolated from the distillates are hæmopyrrole and 2:3-dimethylpyrrole, and from the residue, potassium acetate. The acetic acid must come from the portion of the hæmatopyrrolidinic acid which yields the 2:3-dimethylpyrrole, as the zinc compound of Kuster's hæmatic acid yields the acid $NH<\begin{matrix}CO\cdot CMe\\ CO\cdot C\cdot CH_2\cdot CH_2\cdot CO_2H\end{matrix}$ on oxidation, and this cannot be derived from hæmopyrrole. The formula suggested for hæmatopyrrolidinic acid is therefore

$$NH<\begin{matrix}CMe:CMe\\ CH=C\cdot CH(CH_2\cdot CO_2H)\end{matrix}\cdot\begin{matrix}NH\cdot CMe\\ C=CMe\end{matrix}>CEt.$$

The constitution of the 2:3-dimethylpyrrole has been proved by the following method. The base yields methylmaleinimide, m. p. 105°, when oxidised by Willstätter and Asahina's method (Abstr., 1910, i, 499), and cannot therefore be an ethylpyrrole, 2:5-dimethyl- or 3:4-dimethyl-pyrrole, and, as it does not yield a crystalline azo-dye, cannot be 2:4-dimethylpyrrole (Marchlewski and Robel, Abstr., 1910, i, 206).

It is suggested that hæmin and hæmatin contain a group somewhat similar to that of hæmatopyrrolidinic acid (annexed formula).

On reduction, the 6-carbon ring can become ruptured at carbon atom No. 1 or 2. In the first case hæmatopyrrolidinic acid would be formed, and in the latter an isomeric acid. It is probable that the small yield of hæmatopyrrolidinic acid obtained when hæmatoporphyrin is fused with potassium hydroxide is due to the formation of this isomeric acid.



The authors agree with Küster that the hæmins obtained from different sources have the same composition, and the product described by von Zeyneck (Abstr., 1900, i, 711) as having the composition $C_{34}H_{34}O_4N_5FeCl$ is shown to be impure hæmin, and, after purification by Schalfeeff's method, has the composition of hæmin. The formula suggested is $C_{34}H_{33}O_4N_4FeCl$. The conversion of hæmin into hæmatin by means of alkali is usually regarded as due to the replacement of chlorine by hydroxyl. In further support of this view, it is now shown that hæmatin can be quantitatively transformed back into hæmin by adding a solution of the latter in chloroform containing quinine to a

hot glacial acetic acid solution of sodium chloride and stirring; after repeating the above operations, steel-blue, glistening crystals of pure hæmin are obtained (compare also Siewert, Abstr., 1908, i, 486), and as hæmin can be obtained from hæmatin prepared from hæmin or from oxyhæmoglobin, it follows that the products obtained from the two sources are identical.

According to Nencki and Zaleski (Abstr., 1900, i, 709), hæmin contains two phenolic hydroxyl groups, as it can give dialkyl ethers which are insoluble in alkalis; these hydroxyl groups are also present in hæmatin, although, so far, hæmatin ethers have not been prepared. Hæmatin contains a third hydroxyl group, which is readily replaced by chlorine. This hydroxyl group is removed when the iron is withdrawn from the hæmatin molecule, and is, therefore, presumably attached to the iron atom. Hæmatin and hæmin do not appear to contain free carboxyl groups, but when the iron is removed from hæmin, the product, hæmatoporphyrin, is both distinctly acidic and basic, as it dissolves readily in both dilute acids and alkalis and forms well-defined salts. The development of basic properties is attributed to the removal of the iron which was previously attached to nitrogen, and the production of basic imino-groups. The iron in the hæmin molecule is thus in the tervalent condition, and when removed by the aid of hydrogen bromide, it is removed as ferric salt only, provided the temperature is not allowed to rise.

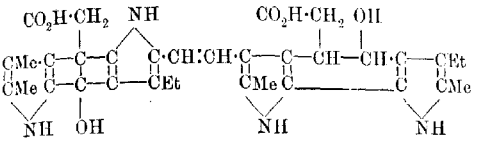
Küster's statement that a ferrous salt is formed is due to the fact that he used comparatively high temperatures, and the ferrous salt obtained was a secondary product formed by the reduction of the ferric salt. The authors used a modification of Nencki and Sieber's method for transforming hæmin into hæmatoporphyrin. Iron hæmatoporphyrin is regarded as the ferric salt of a carboxylic acid, and analyses agree fairly well with the formula $(C_{34}H_{33}O_5N_4)_3Fe$.

In the conversion of hæmin into hæmatoporphyrin, it is suggested that the carboxylic groups which were latent in hæmin become active. The presence of ethylene linkings in hæmatoporphyrin is proved by the readiness with which it is reduced by sodium amalgam, one molecule of the compound taking up 6 or 8 atoms of hydrogen; the solution of the leuco-base thus obtained reduces Fehling's solution and ammoniacal silver nitrate, and on the addition of acids yields a white precipitate of the leuco-base, which immediately turns brown on exposure to the air. The leuco-base cannot be obtained pure, but on oxidising the reduced solution by means of atmospheric oxygen and then acidifying, a product is formed which is apparently identical with deoxyhæmatoporphyrin. The production of this compound from hæmatoporphyrin probably takes place according to the equations: $C_{34}H_{38}O_6N_4 + 8H = C_{34}H_{44}O_5N_4 + H_2O$ and $C_{34}H_{44}O_5N_4 + 3O = C_{34}H_{38}O_5N_4 + 3H_2O$.

Schalfeeff's method for the preparation of hæmin has been modified in several details, and a yield of 7·33 grams has been obtained from 1 litre of blood.

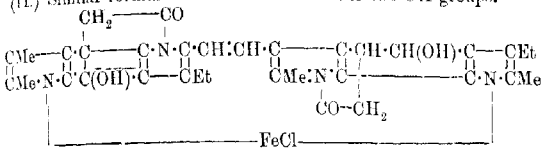
The following structural formulæ are suggested for hæmatoporphyrin (I), mesoporphyrin (II), and hæmin (III).

pi



(I.)

(II.) Similar formula with 2H atoms for the two OH groups.



(III.)

Attention is drawn to the fact that these formulæ cannot be regarded as established beyond question, as they are based to a large extent on the reactions of hæmatopyrrolidinic acid, a compound which it is impossible to obtain in a pure state. J. J. S.

Hæmin Dimethyl Ether. William Küster (*Ber.*, 1910, **43**, 2960—2962).—Hæmin dimethyl ether (Nencki and Zaleski, Abstr., 1900, i, 710) is easily prepared in quantity by adding hæmin dissolved in chloroform containing a little pyridine to a boiling mixture of methyl alcohol and strong hydrochloric acid. It is a black powder consisting of aggregates of microscopic needles, and dissolves in pyridine, probably with the formation of a dimethyl ether of hæmin-pyridinium chloride. On the addition of water, a colloidal solution is formed, from which the dye is precipitated by a few drops of nitric acid, chlorine remaining in the solution. E. F. A.

The Decomposition of Blood-pigment. Compounds of Pyridine in Blood-pigment. Ernst Kalmus. **Pyridine Compound of Hæmochromogen.** Richard von Zeynek (*Zeitsch. physiol. Chem.*, 1910, **70**, 205—216, 217—223, 224—229).—On heating oxyhæmoglobin with 10% alkali, the fluid first shows the spectrum of alkali-hæmatin, and on prolonged heating, of hæmochromogen. Proofs are adduced that this is really hæmochromogen, and not an alkali compound of that substance. In carbon monoxide hæmochromogen, the gas is less firmly combined than it is in carboxyhæmoglobin; it can be removed in a vacuum at room temperature by boiling, or by a stream of pure hydrogen. An apparatus is also described for obtaining the gases evolved on the heat coagulation of blood-pigment.

The two last papers agree in regarding the crystals obtained by the action of pyridine on blood-pigment as a pyridine compound of hæmochromogen, and not as Kobert and Dilling state, as hæmochromogen itself. Dilling's statement that hæmochromogen does not give the guaiacum reaction is also said to be incorrect. W. D. H.

Valency of the Metal in Blood-pigments, and the Estimation of the Gas Combining Power. A Critical Study. WILHELM MANCHOT (*Zeitsch. physiol. Chem.*, 1910, **70**, 230—249).—Kuster states that hæmoglobin and hæmochromogen are ferrous compounds, and bases his conclusion partly on Hüfner's investigations on the uptake of nitric oxide by solutions of metallic salts. The bulk of the present paper is occupied in showing that Hüfner's method is not trustworthy, that hæmoglobin is a ferric compound, and that in hæmocyanin the copper is probably present in the cupric state.

W. D. H.

Yeast Nucleic Acid. III. PHŒBUS A. LEVENE and WALTER A. JACOBS (*Ber.*, 1910, **43**, 3150—3163. Compare Abstr., 1909, i, 620, 686).—On hydrolysing yeast nucleic acid with mineral acids, the following components have been obtained: adenine, guanine, cytosine, uracil, *d*-ribose, and phosphoric acid, but it was not certain whether cytosine and uracil are primary decomposition products or formed by the decomposition of the purine bases.

It is now shown that cytosine is not derived from the purine bases, and that it is not fixed in the nucleic acid molecule as a pentoside. On partial hydrolysis of nucleic acid with ammonia, *cytidine*,

$$C_9H_{13}O_5N_3,$$

is obtained; it forms crystalline derivatives; thus the *picrate* has m. p. 185—187°, the *sulphate*, m. p. 233°, the *hydrochloride*, m. p. 218°. The free base has $[\alpha]_D^{20}$ +19·14°, the *sulphate* having $[\alpha]_D^{20}$ +29·7°.

Cytidine is hydrolysed to cytosine only by concentrated acids or by heating under pressure; neither pentose nor lævulic acid is formed, yet cytidine gives a faint orcinol reaction.

A crystalline acetyl derivative could not be obtained. The *tribenzoyl* derivative crystallises in long, prismatic needles, m. p. 205°; it could not be acetylated.

Nitrous acid effects the quantitative elimination of the amino-group from cytidine, and *uridine* is obtained, crystallising in long, prismatic needles, m. p. 165°, $[\alpha]_D^{20}$ +5·15°.

The relation of amino-acid nitrogen to the total nitrogen in nucleic acid is 3 : 15; this figure confirms the presence of uracil in the molecule, since uracil does not contain an amino-group, whilst the other three bases each contain one, so that were uracil absent the relation should be 3 : 13.

By the action of nitrous acid, adenosine is converted into inosine identical with that obtained from carnine. Similarly, guanosine gave xanthosine. E. F. A.

Triticonucleic Acid. PHŒBUS A. LEVENE and FREDERICK B. LA FORGE (*Ber.*, 1910, **43**, 3164—3167).—It is probable that yeast nucleic acid and the triticonucleic acid discovered in wheat embryos by Osborne and Harris (compare also Osborne and Heyl, Abstr., 1908, i, 376) are identical. Triticonucleic acid on partial hydrolysis gives the nucleosides guanosine and adenosine, and also cytidine, that is, the same complexes as were obtained by Levene and Jacobs (Abstr., 1909, i, 620, 686) from yeast nucleic acid. E. F. A.

The Pentose from the Pancreas. PHŒBUS A. LEVENE and WALTER A. JACOBS (*Ber.*, 1910, **43**, 3147—3150).—Polemical. The authors (Abstr., 1909, i, 447, 620) have shown that the pentose in inosic acid, guanylic acid, and yeast nucleic acid is *d*-ribose, the optical antipode of the *l*-ribose synthesised by Alberda van Eckenstein and Blanksma. Rewald (Abstr., 1909, i, 858) identifies the pentose as xylose. Nucleoprotein prepared from the pancreas by Salkowski's method is now shown to give ribose and no trace of xylose (compare Neuberg, Abstr., 1909, i, 686). E. F. A.

The Pentose from the Pancreas. CARL NEUBERG (*Ber.*, 1910, **43**, 3501—3502).—In reply to Levene and Jacobs' criticism (preceding abstract) of his work (Abstr., 1909, i, 686), the author points out that their process does not determine whether different nucleic acids and pentoses occur in the pancreas, and also calls attention to the many contradictory statements of Levene concerning the pancreas nucleic acid. C. S.

The Pentose from the Pancreas. BRUNO REWALD (*Ber.*, 1910, **43**, 3502—3503).—Levene's identification of the pentose from the nucleic acid of the pancreas, guanylic acid, and similar nucleic acids as *d*-ribose depends on the rotation of a very dilute solution of its osazone (Levene and Jacobs, above). In the author's experiments (Abstr., 1909, i, 858) more than a gram of material was used. C. S.

Prolylglycineanhydride Formed by the Tryptic Digestion of Gelatin. PHŒBUS A. LEVENE (*Ber.*, 1910, **43**, 3168—3170).—Prolylglycineanhydride, $[\alpha]_D$ −55°, was obtained by the tryptic digestion of gelatin extending over eight months (Levene and Beatty, Abstr., 1906, i, 718), whereas the same peptide obtained synthetically by Fischer and Reif (Abstr., 1908, i, 1007) had $[\alpha]_D$ −217°. A product obtained after twenty-four days' tryptic digestion had $[\alpha]_D$ −169°, and the conclusion is drawn that the peptide becomes racemised during the prolonged action of the enzyme. E. F. A.

The Sulphur and Cystine in the Keratin of Birds. HANS BUCHTALA (*Zeitsch. physiol. Chem.*, 1910, **69**, 310—312).—Keratin from goose feathers contains 3·15% sulphur and 6·3% cystine; from hen's claws, 2·28% sulphur and 2·14% cystine; from the epidermic scales of hen's toes, 2·2% sulphur and 1·88% cystine. Hofmann and Pregl (Abstr., 1907, i, 884) state that the horny material from the bird's stomach, which they term koilin, contains no cystine; in the present research it was found to contain rather more than 0·5%. W. D. H.

Iodoproteins. HENRY L. WHEELER and LAFAYETTE B. MENDEL (*Biochem. Zeitsch.*, 1910, **29**, 417—419). CARL NEUBERG (*ibid.* 420—421). —Polemical (compare Abstr., 1910, i, 704, ii, 143). S. B. S.

The Dissociation Constants of Tryptophan. ARISTIDES KANITZ (*Biochem. Zeitsch.*, 1910, **29**, 126—129).—These have been

calculated from the data given for specific rotation of the amphoteric substance, and for the hydrochloride and sodium salts in acid and alkaline solutions. From these, $K_b = 1{\cdot}1 \times 10^{-13}$, and $K_a = 1{\cdot}3 \times 10^{-11}$.

S. B. S.

The Inactivation of Ferments and the Production of Anti-Ferments in vitro in the Presence of Artificial Membranes. A. E. PORTER (*Quart. J. exp. Physiol.*, 1910, 3, 375—390. Compare Abstr., 1910, i, 601).—Certain enzymes can be inactivated by contact with artificial membranes, especially those made of collodion. At the same time the solution acquires inhibitive properties. Possibly in the body, the living membranes act in the same way. Only traces of the enzyme can be recovered from the membrane, the inactivating power of which increases with use. The inhibitive power is only in part due to substances previously in the solution, and the question arises whether the anti-enzyme which appears combines with the enzyme or acts on the substrate as Cramer and Bearn suggest for their zymoids; the latter explanation is adopted as the main one.

W. D. H.

Influence that the Reaction [of the Medium] Exerts on Certain Properties of Malt Macerations. AUGUSTE FERNBACH and M. SCHOEN (*Compt. rend.*, 1910, **151**, 894—897. Compare Abstr., 1906, i, 327; Maquenne and Roux, *ibid.*, i, 327).—The resistance of malt diastases to the action of heat is closely connected with the reaction of the medium in which they are present. If this is rendered neutral to methyl-orange, the amylolytic power of the malt is increased, but the resistance to heat is diminished. On the other hand, the stability is greater in a medium neutral to phenolphthalein, but hydrolytic activity is diminished. Auto-activation is at a maximum when the malt macerations are neutral to phenolphthalein.

W. O. W.

Influence of Different Temperatures on Ferments and on the Regeneration of Fermentative Properties. M. J. GRAMENITZKI (*Zeitsch. physiol. Chem.*, 1910, **69**, 286—300).—Taka diastase in aqueous solutions loses its fermentative properties at 80°, but recovers at temperatures below 45°, slowly at the ordinary temperature, and more quickly at 40°. Similar results were obtained after heating to 115°, the ferment not being destroyed, but only losing temporarily its fermentative power.

The oxydase maltin retains its oxidising power to a slight extent after being heated for ten minutes at 100°. Longer heating (fifteen to twenty minutes) results in complete loss of power for a time; the oxydase recovers its properties, however, after a certain time. When subjected to higher temperatures, the oxydase loses its properties beyond recovery.

At 80° the oxydase not only loses (temporarily) its oxidising properties, but acquires the power of deoxidising.

Solutions of maltin, after being heated for ten minutes at 100°, retain the power of dissolving starch, but no longer produce sugar.

N. H. J. M.

Influence of Temperature on the Activity of Cellase. GABRIEL BERTRAND and ARTHUR COMPTON (*Compt. rend.*, 1910, 151, 1076—1079. Compare Abstr., 1910, i, 212, 290).—The optimum temperature for the hydrolysis of cellose by cellase prepared from sweet almonds is about 46°. The fatal temperature, at which the enzyme is rapidly destroyed, is about 75—76°, but the preparation loses its activity more slowly at lower temperatures. W. O. W

Hydrolysis of Amygdalin by Emulsin. LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1910, 248, 534—535).—The hydrolysis of amygdalin by emulsin occurs in three stages, each of which is caused by a particular enzyme. The amygdalin, under the influence of amygdalase, first yields α-dextrose and mandelonitrileglucoside (Auld, Trans., 1908, 93, 1276); the latter is then decomposed by a β-glucosidase into β-dextrose and *d*-benzaldehydecyanohydrin, which is split by δ-*d*-oxynitrilase into benzaldehyde and hydrogen cyanide.

The new facts on which these statements are based are the following. A 5% solution of emulsin, after being heated for ten hours at 60—65°, hydrolyses *d*-benzaldehydecyanohydrin, but not amygdalin; conversely, the filtrate obtained after saturating a solution of emulsin with magnesium sulphate, hydrolyses amygdalin, but not *d*-benzaldehydecyanohydrin.

The primary formation of *d*-benzaldehydecyanohydrin in the hydrolysis of amygdalin is proved by the fact that the filtrate mentioned above, which cannot contain oxynitrilase or the synthetic enzyme, produces a considerable amount of *d*-benzaldehydecyanohydrin by its action on amygdalin. The view that *d*-benzaldehydecyanohydrin is also produced in a secondary reaction (Abstr., 1910, i, 403) is supported by the fact that *d*-benzaldehydecyanohydrin is produced by the action of emulsin on prulaurasin, a glucoside of the corresponding *i*-nitrile. C. S.

Synthetical Enzyme Action. II. JACOBUS H. VAN'T HOFF (*Sitzungsber. K. Akad. Wiss. Berlin*, 1910, 48, 963—970. Compare Abstr., 1909, ii, 988).—The behaviour of glucosides of tertiary alcohols towards emulsin in presence of their solid products of hydrolysis, and moistened with solutions saturated with these products, has been studied by means of volume changes. Hydrolysis, on account of the taking up of water, is accompanied by contraction; synthesis of the glucoside causes expansion. A small dilatometer was employed. In the case of the hydrolysis of the natural glucosides salicin, arbutin, and æsculin by emulsin, contraction was observed of a magnitude corresponding with the complete hydrolysis of the glucoside. With tertiary alcohol glucosides, emulsin has no synthetic action. This is analogous to the behaviour of the tertiary alcohols on etherification.

Primary alcohols are readily etherified. No glucoside of a solid primary alcohol was available for investigation, but a mixture of dextrose hydrate, glycerol, and emulsin, set aside at 31°, showed a diminution in the amount of dextrose from 0·305 to 0·211 dextrose per gram of the mixture after twenty-five days, and the quantity increased on diluting with an emulsin solution or heating with dilute hydrochloric acid for an hour. With anhydrous dextrose instead of

the hydrate, no condensation was observed. The best results were obtained with a mixture of 2 parts of dextrose hydrate, 4 parts of glycerol, 1 part of water. When used in molecular proportions, about 70% of glycerol and dextrose are converted into glucoside. The rate of synthetic action was proportional to the quantity of enzyme. Of two different enzyme preparations, the most active synthetically was also that most active in promoting hydrolysis. E. F. A.

Isomerisation of Some Phosphorus Compounds. II ALEXANDER E. ARBUSOFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 549—561. Compare Abstr., 1910, i, 802).—The thiophosphinites of the type $PR_2{\cdot}SR'$ under the catalytic influence of alkyl iodides undergo similar processes of isomerisation into the sulphides PSR_2R' to the corresponding oxygen compounds, but in the former the reaction is complicated by the formation of by-products.

Ethyl diphenylthiophosphinite, $PPh_2{\cdot}SEt$, obtained by the action of sodium mercaptide on diphenylphosphoryl chloride, has b. p. 196·5—197°/13 mm., D_0^0 1·1330, and gives double salts with the copper halides, of which the *copper iodide* compound is described. When treated with ethyl iodide in a sealed tube at 100°, it yields *diphenylethylphosphine sulphide*, $PSEtPh_2$, which crystallises in colourless, rhombic tablets, m. p. 65·5—66°; diphenyldiethylphosphonium iodide, PPh_2Et_2I, m. p. 207—208°, the platinichloride of which has m. p. 202—203° (Michaelis, *Annalen*, 1881, **207**, 215, gives m. p. 218°); *ethyl diphenyloxythiophosphinate*, $PPh_2O{\cdot}SEt$, m. p. 72—73°; diphenylphosphinic acid, crystallising in bright prisms, m. p. 194—195°, and probably *ethyl diphenylthiophosphinate*, $PPh_2S{\cdot}SEt$. *iso*Butyl *diphenylthiophosphinite*, $PPh_2{\cdot}S{\cdot}C_4H_9$, was prepared by the action of sodium *iso*butylmercaptide on diphenylphosphoryl chloride. It is a colourless liquid, b. p. 200·5—201°/8 mm., D_0^0 1·0892, and forms a crystalline *additive* compound with copper iodide. Under the catalytic influence of *iso*butyl iodide at 115°, it is converted almost quantitatively into *diphenylisobutylphosphine sulphide*, $PSPh_2{\cdot}C_4H_9$, forming rhombic crystals, m. p. 80—81°, but if the mixture be subjected to prolonged gentle heating at 80°, *diphenyldiisobutylphosphonium iodide*,

$$PPh_2(C_4H_9)_2I,$$

m. p. 183—184°, is obtained. Sodium *iso*amylmercaptide when treated with diphenylphosphoryl chloride forms *isoamyl diphenylthiophosphinite*, $PPh_2{\cdot}S{\cdot}C_5H_{11}$, b. p. 219—220°/12 mm., D_0^{17} 1·0645, which, with *iso*amyl iodide at 120°, yields chiefly *diphenylisoamylphosphine sulphide*, $PSPh_2{\cdot}C_5H_{11}$, large, bright, rhomboid crystals, m. p. 63·5°.

Sodium propylmercaptide with diphenylphosphoryl chloride yields only a small quantity of *propyl diphenylthiophosphinite*, $PPh_2{\cdot}SPr$, b. p. 229—230°/28 mm., which with propyl iodide is rapidly isomerised at 99° into *diphenylpropylphosphine sulphide*, $PSPh_2Pr$, crystallising in thin tablets, m. p. 97—98°. Z. K.

Organic Chemistry.

Formation of Hydrocarbons from Carbon Monoxide. Léo Vignon (*Bull. Soc. chim.*, 1911, [iv], 9, 18—20).—Various observers have shown that when carbon monoxide is passed over heated sodium or potassium hydroxide, soda-lime, or calcium hydroxide, a formate is produced, and that on further heating hydrogen is evolved. In the present investigation it is shown that with lime and carbon monoxide between 350° and 400° considerable quantities of methane, ethylene, and hydrogen are formed, and that from 400° to 600° the quantity of hydrogen increases at the cost of the hydrocarbons. The reactions taking place are probably represented by the following equations:

$$2CO + Ca(OH)_2 = (H\cdot CO\cdot O)_2Ca = C_2O_2(O)_2Ca + H_2;$$
$$2(H\cdot CO\cdot O)_2Ca + CaO = 3CaCO_3 + CH_4;$$
$$4(H\cdot CO\cdot O)_2Ca + 2CaO = 6CaCO_3 + C_2H_4 + 2H_2,$$

and experiments in heating calcium formate or oxalate alone and mixed with lime have confirmed this explanation of the origin of the hydrocarbons. Carbon monoxide may be converted into hydrogen and hydrocarbons to the extent of 99·5% by passage over hot lime several times, and it is suggested that in this way illuminating gas might be freed from this toxic constituent. T. A. H.

A Secondary Heptane in Roumanian Petroleum. N. Costáchescu (*Ann. sci. Univ. Jassy*, 1910, 6, 294—301).—The fraction of petroleum from Colibasi having b. p. 87·5—93·5° contains β-methylhexane with 1 : 3-dimethyl*cyclo*pentane and a small quantity of isomeric heptanes. When the fraction is heated with nitric acid (D 1·4) at 60° in sealed tubes, the β-methylhexane is converted mainly into a *nitro*-derivative, $C_7H_{15}O_2N$, b. p. 86—86·5°/21·5 mm., D_0^0 0·9961, n_D 1·43855; the other hydrocarbons, however, undergo oxidation to oxalic acid and carbon dioxide. W. O. W.

Dimorphism of Iodoform. Bruno Bardach (*Chem. Zeit.*, 1911, 35, 11—12).—The thin, yellow needles obtained previously (Abstr., 1909, i, 645) by the action of iodine and potassium iodide on acetone solutions of anhydrides and anhydride-forming compounds are now found to consist of iodoform. The crystals have m. p. 121°, and, on distilling in steam or crystallising from alcohol, are transformed into the ordinary hexagonal form. F. B.

Estimation of Active Hydrogen in Organic Compounds by means of Magnesium Methyl Iodide. Th. Zerewitinoff (*Ber.*, 1910, 43, 3590—3595. Compare Abstr., 1907, ii, 509; 1908, i, 593).—The method previously described for the determination of replaceable hydrogen atoms is applicable also to the alkaloids. Those alkaloids which contain active hydrogen react with magnesium methyl iodide at the ordinary temperature, and yield methane quantitatively.

When heated, no additional methane is formed, showing the alkaloids to contain no amino-group. The rapidity of the method and the fact that only small quantities of substance are required are important features. A number of the commoner alkaloids were tested.

Pseudo-acids from nitromethane, nitroethane, etc., react as if they contained one hydroxyl, although the amount of methane obtained is somewhat less than the calculated, but it increases on warming. The experiments were made both in amyl ether and in pyridine solution; xylene, mesitylene, and anisole may equally well be used.

E. F. A.

[Pinacolin Derivatives] Corrections. MAURICE DELACRE (*Bull. Soc. chim.*, 1911, [iv], 9, 41—43).—Polemical in reply to Richard (this vol., i, 6), claiming priority as regards the synthesis of the alcohol $CMe_3 \cdot CHMe \cdot OH$ (Abstr., 1906, i, 477) and other matters.

T. A. H.

Preparation of Octan-γη-dione-α-ol and its Homologues. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 227177).—The condensation of unsaturated ketones, by which 1 : 5-diketones are obtained, is a reaction about which very little is known; the diketo-alcohols now described are of technical importance in pharmacological preparations.

Octan-γη-dione-α-ol, $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot OH$, b. p. 142—143°/22 mm., a colourless, odourless oil, miscible with water in all proportions, is prepared as follows: methyleneacetone (Abstr., 1910, i, 652) is mixed with water (15 parts), either alone or in the presence of a small quantity of potassium carbonate, and allowed to remain until the odour of methyleneacetone has disappeared; the solution is acidified with tartaric acid, saturated with ammonium sulphate, and the product extracted with ether, dried, and fractionated, when a considerable amount of butan-γ-on-α-ol, $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot OH$, b. p. 84—85°/23 mm., is also obtained.

βζ-Dimethyloctan-γη-dione-α-ol is prepared by boiling methyl methylene-ethyl ketone with aqueous formic acid during forty to fifty hours, unchanged methyl methylene-ethyl ketone is removed by steam, and the solution rendered alkaline, whereby any *formyldimethyloctandionol* is hydrolysed. The product, a viscous, odourless, colourless oil, b. p. 145·5°/16 mm., 148°/18 mm., and 264—268° under atmospheric pressure, can also be obtained by either boiling dimethyloctendione (this vol., i, 114) with water, or by shaking it with cold dilute formic or with sulphuric acid; the *semicarbazone* has m. p. 209—210°.

F. M. G. M.

Preparation of Narcotics [Glyceryl Ethers]. C. F. BOEHRINGER and SÖHNE (D.R.-P. 226454).—Glyceryl triethyl ether is not a narcotic, but when mixed alkyl residues are introduced, this property is developed; these compounds are colourless, mobile fluids.

Glyceryl αγ-dimethyl β-ethyl ether, $C_7H_{16}O_3$, b. p. 65°/20 mm., D^{20} 0·917, was prepared by the ethylation of the αγ-dimethyl ether in benzene solution with the necessary quantity of sodium ethoxide and

ethyl bromide. *Glyceryl αγ-dimethyl β-propyl ether*, $C_8H_{18}O_3$, was similarly obtained with propyl chloride; it has b. p. 76—77°/17 mm., and D^{20} 0·908. *Glyceryl β-methyl αγ-diethyl ether*, $C_8H_{18}O_3$, has b. p. 75°/17 mm., D^{20} 0·902.

Glyceryl αβ-dimethyl γ-ethyl ether, $C_7H_{16}O_3$, b. p. 49°/7—8 mm., D^{20} 0·919, was prepared from glycerol ethyl ether, methyl iodide, and sodium methoxide in benzene solution.

Glyceryl αγ-diethyl β-propyl ether, $C_{10}H_{22}O_3$, has b. p. 77—78°/9—10 mm., and D^{20} 0·882.

Glyceryl αβ-dimethyl γ-propyl ether, $C_8H_{18}O_3$, b. p. 66—67°/9—10 mm., D^{20} 0·910, was obtained from *glycerol propyl ether*, b. p. 122°/12 mm., D^{22} 1·024, which was prepared by the action of sodium propoxide on glycerol monochlorohydrin.

Glyceryl α-methyl βγ-diethyl ether, $C_8H_{18}O_3$, b. p. 57°/7—8 mm., D^{20} 0·901, was prepared from *glycerol methyl ether*, b. p. 108—109°/8—10 mm., D^{20} 1·115. *Glyceryl β-benzyl αγ-dimethyl ether*, $C_{12}H_{18}O_3$, has b. p. 149—150°/17—18 mm., and D^{20} 1·023. *Glycerol α-ethyl γ-propyl ether*, b. p. 86·5°/10 mm., D^{20} 0·935, was prepared from the sodium derivative of glycerol ethyl ether and propyl bromide, and yielded on methylation *glyceryl β-methyl α-ethyl γ-propyl ether*, $C_9H_{20}O_3$, b. p. 71·5—72°/7—8 mm., D^{20} 0·893. F. M. G. M.

A Very Basic Chromic Acetate. Ernst Gussmann (*Zeitsch. anorg. Chem.*, 1911, **69**, 217—220).—In the preparation of hexa-acetatotripyridinetrichromi-diacetate (Abstr., 1910, i, 503) it was found that the mother liquors contained a violet basic acetate, $Cr_2(OAc)_3(OH)_3,9H_2O$. This is best obtained as follows: To a solution of 10 grams of hexa-acetatotrichromium diacetate (Abstr., 1909, i, 757) in 15 grams of water are added 10 grams of pyridine, and the solution heated for half a day. After separating the crystals of the above-mentioned diacetate of the tripyridine base, the mother liquor is allowed to evaporate at room temperature. After several weeks the crystals are collected, and washed with cold water to remove the admixed diacetate of the tripyridine base. Rapid concentration of the solution is not favourable to the formation of crystals.

The violet acetate forms violet, four-sided double pyramids, and loses $9H_2O$ over sulphuric acid. It readily dissolves in dilute acids, giving a violet solution, which makes it probable that the hydroxyl groups possess an hydroxo- and not an ol-character. In phenol it gives a normal molecular weight. It is also formed when a solution of the diacetate of the trichromium base is repeatedly evaporated, or when a solution of freshly cold-precipitated chromium hydroxide in acetic acid is allowed to evaporate at room temperature.

A green, amorphous basic acetate has also been obtained by drying the diacetate of the hexa-acetatotrichromium base at 100—110°. It is less basic than the violet acetate. A formula cannot be given for it at present. T. S. P.

Behaviour of Acetic Anhydride at a High Temperature. Eugen Bamberger (*Ber.*, 1910, **43**, 3517—3520).—According to the author, the first stage in the formation of acetone, by the distillation

of calcium acetate, is the dissociation of the salt into calcium oxide and acetic anhydride, which at the high temperature necessary for its production decomposes into carbon dioxide and acetone. With a view to confirming this supposition, the behaviour of acetic anhydride at high temperatures has been studied. On heating the anhydride for several hours at 290—300°, small quantities of acetone and acetylacetone were found amongst the products. Whether the formation of the last-named substance is due to the direct acetylation of acetone by means of acetic anhydride, or to the intermediate formation of keten, has not been determined.

These experiments also support the contention of Schmidlin and Bergmann (Abstr., 1910, i, 816) that the first stage in the synthesis of keten from acetic anhydride (Wilsmore, Trans., 1907, 91, 1938) consists in the decomposition of the latter into carbon dioxide and acetone.

The reaction $O(COMe)_2 = CO_2 + COMe_2$ is probably reversible, but the amounts of carbon dioxide and acetone are very small, when equilibrium is attained.

The fact that acetone is produced in large quantity by the distillation of calcium acetate is not in opposition to this view, for the dissociation products, carbon dioxide and acetone, are continuously removed during the reaction, the latter by distillation, the former by union with the calcium oxide, produced by the decomposition of the acetate.

Various by-products obtained in the manufacture of acetone were examined for acetylacetone, but no indication of its presence was obtained. F. B.

Salts of a Green and of a Violet Propionatochromium Base. Rudolf F. Weinland and Karl Hoehn [with M. Fiederer] (*Zeitsch. anorg. Chem.*, 1910, 69, 158—178. Compare Abstr., 1908, i, 847).—Salts of the *green hexapropionatotrichromium* base, $Y(OH)_3$, where $Y = \left[Cr_3\begin{matrix}(O\cdot COEt)_6\\(OH_2)_2\end{matrix}\right]$. To prepare the *dichromate propionate*, $Y(O\cdot COEt)(Cr_2O_7),H_2O$, 2 grams of chromium trioxide are warmed with 20 c.c. of propionic acid. After filtering from the undissolved chromium trioxide, the solution, on keeping, deposits four-sided, brownish-green plates of the salt in question. Molecular weight determinations in acetophenone gave 961—801, as against 937·6. The *sesquichromate propionate*, $Y(O\cdot COEt)(HCrO_4)(\frac{1}{2}CrO_4)$, is obtained by warming chromium trioxide and chromium hydroxide, in the proportion of 2 mols. of the former to 1 mol. of the latter, with propionic acid. On concentrating the solution, dark olive crystals are obtained. Molecular weight in acetophenone was 753—878, as against 877·5. When a mixture of chromium trioxide and chromium hydroxide in the molecular proportion of 1 : 3 is dissolved in propionic acid and the solution concentrated, green, six-sided plates of the *chromate propionate*, $Y(O\cdot COEt)(CrO_4),1{\cdot}5H_2O$, are obtained. It may also be obtained by dissolving 1 gram of chromium trioxide in 50 c.c. of propionic acid and concentrating the solution.

When less than ten parts of propionic acid to one part of chromium

trioxide are taken and the mixture heated, chromates are obtained which contain less propionic acid in the anion than the above-mentioned salts. Whether a dichromate or a lower chromate of the base is obtained depends on the time of heating; the longer the heating, the poorer is the resulting chromate in chromic acid.

Whenever the dichromate propionate is recrystallised from a little water, propionic acid is lost from the anion, and pure *sesquichromate*, $Y(CrO_4)(\frac{1}{2}Cr_2O_4),2H_2O$, is obtained. Even when the chromate propionates are recrystallised from a solution of propionic acid, some of the latter is split off from the anion.

The *chloride chromate*, $Y(CrO_4)Cl,H_2O$, is obtained as yellowish-green, six-sided plates by the addition of concentrated hydrochloric acid to strong solutions of any of the above salts. The *monopropionate*, $Y(O{\cdot}COEt),2H_2O$, is prepared from the chromate propionates by removing the chromic acid with lead propionate, or from the chloride (Abstr., 1908, i, 935) by treatment with silver propionate; it forms pale green, rod-like crystals.

Salts of a *violet pentapropionatotrichromium* base, $Y(OH)_2$, where $Y = Cr_3\begin{matrix}(O{\cdot}COEt)_5\\(OH)_2\\(OH_2)_2\end{matrix}$. The *dipropionate*, $Y(O{\cdot}COEt)_2$, forms the starting point for the preparation of the other salts. It is best prepared by dissolving 1 mol. of freshly-prepared chromium hydroxide, which has been washed with cold water, in 3 mols. of propionic acid at the room temperature. The solution is then heated in a sealed tube for five hours at 140—160°; on cooling, violet crystals of the dipropionate are found on the walls of the tube. After purification by a somewhat complicated method they are obtained as flat prisms, which may be 1 cm. long. Molecular weight in acetophenone was 615, as against 737·7. The *monopropionate*, $Y'(O{\cdot}COEt),3H_2O$, where $Y' = \begin{matrix}(CEtO_2)_5\\Cr_3(OH)_3\\H_2O\end{matrix}$, is obtained by saturating the aqueous solution of the dipropionate with sodium chloride or nitrate; light violet crystals. The *sesquipropionate*, $Y(O{\cdot}COEt)_2,Y'O{\cdot}COEt,H_2O$, results on evaporating a solution of one part of the dipropionate with five parts of sodium propionate; violet, flat prisms. The *sulphate propionate*, $(YO{\cdot}COEt)_2SO_4,4H_2O$, crystallises in violet plates on the addition of concentrated sulphuric acid to the saturated solution of the dipropionate. The *bromide propionate*, $Y(O{\cdot}COEt)Br,4H_2O$, forms violet prisms, as also does the *chloride*, $Y'Cl,Y'O{\cdot}COEt,10H_2O$; they are formed from the dipropionate by precipitation with concentrated hydrobromic and hydrochloric acid respectively.

All the salts of the violet base are readily soluble in ether and chloroform; those of the green base are insoluble in ether. The salts of the violet base cannot be recrystallised from water.

From the solution of chromium chloride hydrate, $CrCl_3,6H_2O$, in a solution of sodium propionate, violet crystals are obtained having the composition $Cr(O{\cdot}COEt)_2{\cdot}OH,H_2O$. They are insoluble in ether, in contradistinction to the violet pentapropionatotrichromium salts.

T. S. P.

Condensation of $a\beta$-Dibromopropaldehyde with Malonic Acid. ROBERT LESPIEAU (*Compt. rend.*, 1910, **151**, 1359—1361. Compare Spenzer, Abstr., 1905, i, 204).—$a\beta$-Dibromopropaldehyde acts on malonic acid to form *$\beta\gamma\delta$-tribromovaleric acid*, m. p. 128—130°; the *ethyl* ester has b. p. 160—161°/12—13 mm. Both the acid and the ester, on treatment with zinc and alcohol, furnish *ethyl Δ^{β}-pentenoate*, $CHMe{:}CH{\cdot}CH_2{\cdot}CO_2Et$, b. p. 145—146°/760 mm. On brominating the corresponding acid, a substance is obtained probably identical with $a\beta$-dibromovaleric acid. W. O. W.

The Oil and Wax of Coffee Beans. HANS MEYER and ALFRED ECKERT (*Monatsh.*, 1910, **31**, 1227—1251).—Unroasted coffee beans, from which the greater part of the caffeine had been extracted, were dried, powdered, and digested with benzene. The oil thus obtained had a brownish-yellow colour, was nearly odourless, and had the consistency of olive oil. On hydrolysis it gave 21·2% of non-saponifiable matter. For isolating the acids formed on hydrolysis, it was found advisable to saponify with lithium hydroxide solution (compare Partheil and Ferié, Abstr., 1904, i, 4), but this method did not give a complete separation of saturated from unsaturated acids. The sparingly soluble lithium salts gave the following acids: Carnaubic acid, 10% (Stürcke, Abstr., 1884, 1280; Darmstädter and Liefschütz, 1896, i, 346; Dunham and Jacobson, 1910, i, 215); daturic acid, 1—1·5% (Gerard, Abstr., 1890, 1396; Kreis and Hafner, 1903, i, 788; Holde, Ubbelohde, and Marcusson, 1905, i, 318); palmitic acid, 25—28%, and decoic acid, 0·5%.

In order to obtain the carnaubic acid pure, the least soluble fraction of the lithium salts was transformed into chloride by means of thionyl chloride and then into ester; the processes of conversion into lithium salt, chloride, and ester were repeated, when the *methyl* ester was obtained in the form of glistening plates, m. p. 54—55°, and this on hydrolysis gave the acid with m. p. 74° (not 70° or 72·5°). The *lead* salt has m. p. 109—110°, and is soluble in toluene. The acid resembles stearic acid in many respects, but its ethyl ester is not so soluble in alcohol. The detection of glyceryl esters of this acid in fats is readily accomplished by warming the fat with absolute alcohol and a little sulphuric acid, when the sparingly soluble ethyl carnaubate mixed with a little palmitate and stearate is deposited.

Methyl daturate, $C_{15}H_{33}{\cdot}CO_2Me$, has m. p. 30°, and the *magnesium* salt, m. p. 137—142°.

The more soluble lithium salts were converted into lead salts, and the saturated and unsaturated acids separated by extraction with benzene. The acids isolated were palmitic, oleic 2%, and linoleic 50%. The unsaturated acids were identified by oxidation with 2% permanganate solution in the cold, when dihydroxystearic and sativic acids were obtained, and by bromination, when tetrabromostearic acid was isolated.

The wax contained a small amount of alkaloid, which was removed by steam distillation and solution in glacial acetic acid. When finely divided and made into an emulsion with potassium hydroxide solution, the wax was oxidised by 4% permanganate to carnaubic acid, and when

hydrolysed with alcoholic potassium hydroxide solution at 150—170°, it gave carnaubic acid (50%) and a compound with the properties of a tannol. This latter has not been obtained crystalline; it has no definite m. p., but is soluble in alkali solutions and can be benzoylated. The wax is therefore a tannol resin. J. J. S.

Preparation of Compounds of Unsaturated Acids with Aldehydes, Ketones, and Formic Acid. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 226222 and 226223).—It is found that unsaturated fatty acids of high molecular weight combine (in the presence of acid condensing agents) with ketones or aldehydes to form a new series of oily compounds. The free acid may be replaced by the oil, which under the experimental conditions becomes almost entirely hydrolysed. The substances employed were acetone, formaldehyde, acetaldehyde, benzaldehyde, dextrose, lævulose, sucrose, and maltose, which were severally heated with castor oil, ricinoleic acid, oleic acid, and cottonseed oil in the presence of either sulphuric acid, zinc chloride, or phosphoryl chloride. The second patent states that formic acid may be employed in this reaction instead of formaldehyde, and details are given of its condensation with ricinoleic acid.

F. M. G. M.

Preparation of Acyl Derivatives of Castor Oil [Ricinoleic Acid]. VEREINIGTE CHININFABRIKEN ZIMMER & CO. (D.R.-P. 226111. Compare Abstr., 1909, i, 696).—The aromatic acyl derivatives of ricinoleic acid have not previously been prepared; it is now found that aromatic acid chlorides reacting with the hydroxyl group of the acid yield the corresponding acyl derivative; these are usually tasteless, odourless oils.

The *benzoyl* ester was prepared by boiling castor oil in benzene solution with benzoyl chloride in the presence of pyridine during half an hour; the *anisoyl* ester was obtained in a similar manner. The *salicyl* ester was prepared by heating castor oil and salol together at a temperature of 200° during three hours, and distilling off the separated phenol in a vacuum. F. M. G. M.

Ester Condensations with Chloroacetic Ester. WILHELM WISLICENUS (*Ber.*, 1910, 43, 2528—2533).—In the Claisen condensation, ethyl chloroacetate can function as the ester component and also as the methylene compound.

The interaction of ethyl chloroacetate, ethyl oxalate, and sodium ethoxide in ethereal solution yields ethyl chloro-oxalacetate,

$$CO_2Et\cdot CO\cdot CHCl\cdot CO_2Et,$$

b. p. 150—152°/56 mm. (compare Peratoner, Abstr., 1893, i, 11; Roubleff, Abstr., 1891, 223); this forms a green *copper* salt, and yields oxamide when treated with ammonia; at 240° it loses only half the theoretical amount of carbon monoxide; in alcoholic solution it gives an intense red ferric chloride reaction.

When equal molecular quantities of ethyl formate and ethyl chloroacetate are introduced into a cold alcoholic ethereal solution of potassium methoxide, a *potassium* salt is formed, from which, by

acidification, *ethyl α chloroformylacetate*, $CHO\cdot CHCl\cdot CO_2Et$, is obtained as an oil giving an intense violet ferric chloride reaction. On repeated distillation in a vacuum, it is obtained in colourless leaflets, m. p. 88—90°; the latter give only a faint violet coloration with ferric chloride, and yield with copper acetate a green *copper* salt; after fusion, the crystalline ester gives the original, intense violet ferric chloride reaction. The isomerism here exhibited has not been further investigated, but there is little doubt that the liquid ester has the enolic structure, $OH\cdot CH{:}CCl\cdot CO_2Et$.

The *benzoyl* derivative, $OBz\cdot CH{:}CCl\cdot CO_2Et$, prepared from the above-mentioned potassium salt, crystallises from alcohol in large, colourless plates, m. p. 90—91°. With phenylhydrazine, both the ester and the potassium salt react to form the osazone of ethyl β-hydroxypyruvate, $CH(:N\cdot NHPh)\cdot C(:N\cdot NHPh)\cdot CO_2Et$ (compare Will, Abstr., 1892, 356).

The condensation of two molecules of ethyl chloroacetate has also been effected (compare Erlenbach, Abstr., 1892, 953); ethyl chloroacetate (2 mols.) and sodium ethoxide (1 mol.), free from alcohol, are allowed to react in ethereal solution at a low temperature; on acidifying the *sodium* salt thus produced, *ethyl α-γ-dichloroacetoacetate*, $CH_2Cl\cdot CO\cdot CHCl\cdot CO_2Et$, is obtained in an impure condition. It is purified by converting it into the copper salt and decomposing this with hydrochloric acid; it forms a colourless oil with a penetrating odour, b. p. 118—120°/15 mm., and solidifies on cooling, m. p. 18—20°; it gives an intense cherry-red coloration with ferric chloride, and is hydrolysed by boiling with dilute sulphuric acid to *s*-dichloroacetone; the *copper* salt, $(CH_2Cl\cdot CO\cdot CCl\cdot CO_2Et)_2Cu$, crystallises in microscopic, green needles, melting at 149° (decomp.) to a turbid yellow liquid. F. B.

Ethyl γ-Chloroacetoacetate. Robert Lespieau (*Bull. Soc. chim.*, 1911, [iv], 9, 31—33. Compare Abstr., 1899, i, 243; 1905, i, 406; Pieh, Abstr., 1907, i, 178).—Polemical with Schlotterbeck (Abstr., 1909, i, 550) on the physical properties of this ester. T. A. H.

Condensation of Ethyl Acetate with its Higher Homologues. André Wahl (*Compt. rend.*, 1911, 152, 95—98).—It has hitherto been found impossible to prepare β-ketonic esters by condensing ethyl acetate with its higher homologues. This condensation has now been effected by adding alternately to the higher ester, small, carefully weighed portions of ethyl acetate and sodium. In this way the formation of ethyl acetoacetate and of the compound

$$R\cdot CO\cdot CHR\cdot OH$$

is prevented or diminished; the yield, however, is small, 5—6% in the case of ethyl propionylacetate for the pure compound, and 18—20% in the case of ethyl butyrylacetate. The latter forms a green *copper* derivative, $Cu(C_8H_{13}O_3)_2$, m. p. 125—126°; on boiling with methyl alcoholic changes into a blue *basic* salt, $C_8H_{13}O_3\cdot CuOMe$.

Ethyl butyrylacetate is converted by oxides of nitrogen into *ethyl butyrylglyoxylate*, $CH_2Et\cdot CO\cdot CO\cdot CO_2Et$, an orange-yellow liquid, b. p.

87—88°/13 mm., becoming colourless on the addition of water or alcohol, with which it combines; the diketone condenses with *p*-phenylenediamine, forming *ethyl* 2-*propylquinoxaline*-3-*carboxylate*,

$$C_6H_4<\begin{matrix}N{:}CPr^{\alpha}\\ |\\ N{:}C{\cdot}CO_2Et\end{matrix}$$

long needles, m. p. 63—64°. W. O. W.

γ-Ethoxy-α-alkylacetoacetic Esters. Marcel Sommelet (*Bull. Soc. chim.*, 1911, [iv], **9**, 33—38. Compare Abstr., 1907, i, 21, 107).—The considerable differences in the boiling points ascribed by Isbert to the compounds he regarded as α-ethoxybutanone and α-ethoxypentanone (Abstr., 1886, 1009) from those found by the author for his preparations of these substances has led him to re-investigate esters having the constitution assigned by Isbert to the esters from which his ketones were prepared. The author finds that they do not correspond with Isbert's descriptions, and that on hydrolysis they furnish ketones identical with those he has described already (*loc. cit.*).

Ethyl γ-ethoxy-α-methylacetoacetate, $OEt{\cdot}CH_2{\cdot}CO{\cdot}CHMe{\cdot}CO_2Et$, D_4^0 1·033, D_4^{17} 1·017, b. p. 112—114°/14 mm., 116·5—118·5°/19 mm., obtained by condensing ethoxyacetonitrile with ethyl α-bromopropionate in presence of zinc (compare Blaise, Abstr., 1901, i, 252), is a faintly yellow liquid, which reduces ammoniacal silver nitrate in the cold, and gives a violet coloration with ferric chloride. On hydrolysis with potassium hydroxide solution, the ester yields α-ethoxybutanone, and with hydrazine hydrate gives a *pyrazolone*, m. p. 135—137°, which crystallises from boiling water.

Ethyl γ-ethoxy-α-ethylacetoacetate, D_4^{15} 1·0157, b. p. 125—128°/18 mm., similarly obtained, resembles its lower homologue, and on hydrolysis gives α-ethoxypentanone, and with hydrazine hydrate furnishes a *pyrazolone*, m. p. 99—99·5°, which crystallises from boiling water in hard prisms.

Ethyl γ-ethoxy-αα-dimethylacetoacetate, D_4^0 1·065, D_4^{17} 1·047, b. p. 114—116°/17 mm., 111—113°/14 mm., obtained by condensing ethyl bromo*iso*butyrate with ethoxyacetonitrile in presence of zinc, is a pale yellow liquid, reduces ammoniacal silver nitrate, and on alkaline hydrolysis furnishes *ethoxymethyl* iso*propyl ketone*, $OEt{\cdot}CH_2{\cdot}COPr^{\beta}$, b. p. 160° (approx.), which gives a *semicarbazone*, m. p. 128—129·5°. Along with the ester there is formed in this condensation a small quantity of a *substance*, $C_{12}H_{19}O_4N$, m. p. 90—91·5°, which crystallises in needles or prisms, is soluble in strong acids, becomes yellow in contact with alkali, and gives no coloration with ferric chloride. Heated with alkali in a closed tube, it evolves ammonia and furnishes a trace of *iso*butyric acid and an unidentified oily product.

T. A. H.

Iso- and Hetero-poly-acids. II. Oxalato-tellurates. Arthur Rosenheim and M. Weinheber (*Zeitsch. anorg. Chem.*, 1911, **69**, 261—265. Compare this vol., ii, 116).—Concentration of a solution containing molecular proportions of telluric acid and an alkali oxalate leads to the deposition of crystals of the oxalato-tellurates. The potassium, rubidium, and cæsium salts have the general formula

$M_2C_2O_4,H_6TeO_6$, where M = K, Rb, or Cs, and crystallise in stellar aggregates of needles. The effect of heat on these salts shows that the water is firmly combined, so that telluric acid hydrate, H_6TeO_6, and not the anhydride, TeO_3, is probably contained in the complex anion. These compounds should therefore be formulated as

$$M_2[H_6TeO_6C_2O_4].$$

Their solubilities increase from the potassium, through the rubidium, to the cæsium salt, this being the opposite order to what generally obtains with salts of these metals. Comparison of the solubility of the potassium salt with the solubilities of potassium tellurate and oxalic acid shows that a great diminution in solubility has taken place, pointing to complex formation. This could not be verified by conductivity measurements, however, owing to the hydrolysis which takes place.

Homogeneous ammonium or sodium oxalato-tellurates could not be obtained. T. S. P.

Molecular Rearrangements in the Camphor Series. VI. *iso*Campholactone. WILLIAM A. NOYES and A. W. HOMBERGER (*J. Amer. Chem. Soc.*, 1910, 32, 1665—1669).—In an earlier paper (Abstr., 1909, i, 133) the authors described a compound obtained by the action of nitric acid on *iso*campholactone, which they regarded as a dilactone of the composition $C_8H_{13}O_4$. It has now been found that this substance is, in reality, a nitrolactone.

*iso*Campholactone, prepared by Noyes and Taveau's method (Abstr., 1904, i, 807), gave $[\alpha]_D^{25}$ −63·1° in an 8·8% solution in alcohol; Noyes and Taveau found $[\alpha]_D$ −60·7° in a 5% solution.

On heating *iso*campholactone with ammonium hydroxide in a sealed tube at 100°, it yields the *ammonium* salt of the corresponding acid, m. p. 137°, which is re-converted into the lactone when left in the air. When the lactone is heated with nitric acid (D 1·27), a mixture of products is obtained, the chief of which is *nitroisocampholactone*, $NO_2\cdot C_8H_{13}\langle{}^{CO}_{O}{}^{|}$, m. p. 122°, b. p. 272°, which crystallises in needles, and has $[\alpha]_D$ −85·4° in a 5·5% solution in alcohol. A monobasic lactonic *acid*, $C_9H_{12}O_4$, m. p. 138°, was isolated from the mother liquor, which has $[\alpha]_D$ −42·05° in a 6% solution in alcohol; its *barium* salt was prepared; the *amide* has m. p. 164°.

Aminoisocampholactone, $NH_2\cdot C_8H_{13}\langle{}^{CO}_{O}{}^{|}$, m. p. 84°, obtained by reducing nitro*iso*campholactone with tin and hydrochloric acid, forms small crystals, and is decomposed by sodium hydroxide with formation of a compound, m. p. 152°. *Hydroxylaminoisocampholactone*,

$$OH\cdot NH\cdot C_8H_{13}\langle{}^{CO}_{O}{}^{|},$$

m. p. 144°, prepared by treating nitro*iso*campholactone with zinc dust and acetic acid, forms small, stellate crystals, is slightly basic, and readily reduces Fehling's solution.

When nitro*iso*campholactone is shaken with 0·5*N*-sodium hydroxide until completely dissolved, and afterwards acidified with hydrochloric

acid, an *acid*, $C_5H_8O_2N\cdot CO_2H$, m. p. 73—74°, is produced; its *barium* salt crystallises in needles containing $2\frac{1}{2}H_2O$. By the action of ammonium hydroxide on nitro*iso*campholactone, the corresponding *amide*, m. p. 96—97°, is obtained. E. G.

Molecular Rearrangements in the Camphor Series. VII. Derivatives of *iso*Camphoric Acid; *l*-Hydroxydihydrocampholytic Acid. William A. Noyes and Luther Knight (*J. Amer. Chem. Soc.*, 1910, 32, 1669—1674).—*d*- and *l-iso*Camphoric acids are usually regarded as *cis*- and *trans*-isomerides. As, however, the evidence of this structure does not seem altogether conclusive in the case of the latter compound, the present work was undertaken in order to throw some light on the question. Assuming that *iso*camphoric acid is stereoisomeric with camphoric acid, α is used in this paper to denote the secondary carboxyl, and β the tertiary carboxyl, group.

By boiling *iso*camphoric acid with methyl alcohol and sulphuric acid, the α-methyl and dimethyl esters are obtained. The *dimethyl* ester, $C_8H_{14}(CO_2Me)_2$, b. p. 146°/27 mm., has D^{20} 1·073, D^{23} 1·069, and $[\alpha]_D^{20}$ −65·2°; a 10% solution in alcohol has $[\alpha]_D$ −65·6°. The *α-methyl* ester, m. p. 88°, crystallises in needles, and gives $[\alpha]_D$ −57·9° in a 10% alcoholic solution; its *amide*, m. p. 157°, crystallises in plates, and has $[\alpha]_D$ −60·05° in a 10% alcoholic solution.

*β-iso*Camphoramic acid, $CO_2H\cdot C_8H_{14}\cdot CO\cdot NH_2$, m. p. 165—166°, obtained by hydrolysing the α-methyl ester amide with sodium hydroxide, crystallises in needles. When its sodium salt is treated with sodium hypobromite solution, *amino*iso*dihydrocampholytic acid*, $CO_2H\cdot C_8H_{14}\cdot NH_2$, m. p. 225—227°, is produced; its *hydrochloride* and *lead* salt are described. When this acid is heated at 250—300°, it is converted into an *anhydride*, which furnishes a *nitroso*-compound, m. p. 194°. If aminoisodihydrocampholytic acid hydrochloride is treated with a solution of sodium nitrite, there are produced a hydrocarbon, a lactone, *d*-campholytic acid, and *l-hydroxydihydrocampholytic acid*, $CO_2H\cdot C_8H_{14}\cdot OH$, m. p. 132°, which forms granular crystals and gives $[\alpha]_D$ −70·04° in an aqueous solution containing 1·45%. The formation of this compound, instead of hydroxydihydroisocampholytic acid, which was expected, renders it probable that the former is the more stable, and that part of the hydroxydihydroisocampholytic acid is converted into it by the action of the nitrous acid, or else that *d*-campholytic acid is formed as an intermediate product and unites with water to produce *l*-hydroxydihydrocampholytic acid. E. G.

Saccharinic Acids. Heinrich Kiliani (*Ber.*, 1911, 44, 109—113).—A reply to Nef (Abstr., 1910, i, 714). The phenylhydrazide of α-metasaccharin has m. p. 145°, as previously found, and not 113—115°, as stated by Nef.

The trihydroxyadipic acid described by Kiliani and Eisenlohr (Abstr., 1909, i, 553) is not identical with the old trihydroxy-acid; it has m. p. 159—160°, whereas a mixture of the two melts at 142—145°. The silver salt also does not crystallise in the small plates characteristic of the silver salt of the old acid. The presence of

a compound with a branched chain in parasaccharin has been confirmed by reduction to α-ethylbutyrolactone, and the isolation of this in the form of Chanlaroff's calcium salt, $3Ca(C_6H_{11}O_3)_2,2H_2O$ (Abstr., 1885, 374). The yield of calcium salt, however, is small, and large quantities of syrupy salts are formed.

By oxidising parasaccharin with nitric acid to parasaccharone (Abstr., 1904, i, 975) and reducing this with hydriodic acid, a small amount of *n*-adipic acid has been obtained. These results indicate that parasaccharin must be a mixture.

Nef's parasaccharin (*α-d*-galactometasaccharin) does not appear to be hygroscopic, whereas the author's preparations are excessively hygroscopic.

The acid obtained by the oxidation of barium parasaccharinic acid is not hydroxycitric acid, as stated previously (Abstr., 1904, i, 976), but *l*-tartaric acid. J. J. S.

Glucodeconic Acids. L. H. Philippe (*Compt. rend.*, 1910, 151, 1366—1367. Compare this vol., i, 12).—On evaporating an aqueous solution of *β*-glucodeconic acid, a mixture of two compounds is obtained: (1) the hydrated *β-lactone*, $C_{10}H_{18}O_{10},H_2O$, crystallising in hemihedral needles, m. p. 135° (anhydrous, m. p. 193°), $[\alpha]_D^{17}$ −41·2°; (2) an *anhydride*, $C_{20}H_{38}O_{21}$, separating in microscopic granules resembling those of starch, m. p. 216—218°, $[\alpha]_D$ about −10°. The lactone is the chief constituent in dilute solutions, whilst the anhydride predominates in concentrated solutions. The *β*-lactone is also formed when the α-lactone is heated at 140° in pyridine.

Sodium β-glucodeconate is gummy, but the *barium*, *cadmium*, and *strychnine* salts are crystalline. The *β-phenylhydrazide* crystallises in needles, m. p. 246°, and is ten times more soluble in water than the α-compound. W. O. W.

Derivatives of Aldol and Crotonaldehyde. Rudolf Wegscheider and Ernst Späth (*Monatsh.*, 1910, 31, 997—1029).—The authors have examined the behaviour of aldol towards acetylating agents under various conditions, and find that acetylation is accompanied by the formation of condensation products; loss of water and rupture of the aldol molecule also occur.

When aldol is boiled with acetic anhydride in the presence of a little sulphuric acid, ethylidene acetate and *aldol triacetate*,

$$OAc\cdot CHMe\cdot CH_2\cdot CH(OAc)_2,$$

are produced. The latter substance is a colourless oil, b. p. 138—140°/12 mm., which yields crotonaldehyde when boiled with water or alkalis; when treated with bromine in chloroform solution, it is converted into bromocrotonaldehyde.

Gentle acetylation of aldol with acetic anhydride and sulphuric acid in benzene or chloroform solution yields, amongst other products, *aldol monoacetate*, $OAc\cdot CHMe\cdot CH_2\cdot CHO$; it is a colourless oil, b. p. 87—89°/18 mm., and is also obtained by the action of acetic acid and a little sulphuric acid on aldol at the ordinary temperature.

By heating aldol with acetic anhydride alone, Wurtz (this Journ., 1872, 808) obtained two substances, which he considered to be croton-

dehyde diacetate and acetylaldol. The authors have repeated Wurtz's periments, and find that his crotonaldehyde diacetate consists of a ixture of aldol triacetate and a compound $C_{12}H_{18}O_5$, whilst the ibstance described as acetylaldol is identical with crotonaldehyde acetate. The *compound*, $C_{12}H_{18}O_5$, is probably the diacetyl deriv- ive of dialdan, $C_8H_{14}O_3$, a substance obtained by Wurtz by the tion of acids on aldol; it is produced by gently acetylating aldol ith acetic anhydride and sulphuric acid, either alone or in chloroform nd benzene solution, and also by the action of acetic and sulphuric ids on aldol at the ordinary temperature; the b. p. varies from 44—147°/13 mm. to 152—154°/12 mm., according to the method of reparation, but whether this variation is due to impurity or the resence of two dialdan diacetates has not been decided. The onstitution of the compound is discussed, and arguments advanced in avour of the formula OAc·CHMe·CH(CHO)·CH(OAc)·CH:CHMe.

The following condensation products were also isolated and xamined: a *diacetate* of $C_{12}H_{20}O_5$, colourless oil, b. p. 201—203°/ 0 mm., produced by acetylating aldol with acetic anhydride in the resence of a little sulphuric acid, and probably having the structure $CHMe\cdot O\cdot CHMe\!>\!C\!<\!\begin{matrix}CHO\\ CH(OAc)\cdot CH:CHMe\end{matrix}$; a *substance*, $C_{18}H_{30}O_7$, . p. 228—233°/13 mm., obtained by the action of a mixture of acetic nd sulphuric acids on aldol, and represented as a monoacetyl erivative of $OH\cdot CHMe\cdot CH(CHO)\cdot CH(OH)\!>\!C\!<\!\begin{matrix}CHMe\text{———}O\\ CH(OH)\cdot CH_2\cdot CHMe\end{matrix}$; mixture of the monoacetyl derivatives of $C_8H_{14}O_3$ and $C_8H_{16}O_4$, roduced by acetylating aldol with acetic anhydride and sulphuric cid in chloroform solution.

Acetyl chloride reacts with aldol in benzene solution, forming -chlorocrotyl acetate, CHMe:CH·CHCl·OAc, b. p. 76—77°/18 mm.; he same substance is also produced by the addition of acetyl chloride to crotonaldehyde. When aldol is acetylated by means of acetic anhydride in the presence of sodium acetate, the main product is rotonaldehyde diacetate.

Aldolphenylhydrazone is obtained in an impure condition by the action of phenylhydrazine on aldol in ethereal solution; it is a viscid oil, b. p. 196°/10 mm.; the *p-nitrophenylhydrazone* crystallises in reddish-yellow needles, m. p. 109—111°, with previous sintering at 107°; *aldoloxime* has b. p. 117—118°/11 mm.

Crotonaldehydephenylhydrazone, prepared by the action of phenyl- hydrazine on crotonaldehyde in alcoholic solution at 35—42°, is a yellow oil, b. p. 156—158°/11 mm. (compare Trener, Abstr., 1901, i, 232); the p-*nitrophenylhydrazone* crystallises in brown needles, m. p. 184—185°.

The authors also describe two new condensation products of acetaldehyde. A specimen of crotonaldehyde, which had been kept for three and a-half months in a closed glass vessel filled with carbon dioxide, yielded on distillation an *oil*, $C_{16}H_{28}O_4$, b. p. 88—95°/16 mm., and a viscid *liquid*, $C_{16}H_{28}O_6$, b. p. 156—161°/16 mm. It is suggested

that these two substances are produced by the condensation of acetaldehyde, derived from the para-aldehyde (with which the original crotonaldehyde was probably contaminated) according to the equations: $C_{10}H_{18}O_4 = 5C_2H_4O - H_2O$ and $C_{16}H_{28}O_6 = 8C_2H_4O - 2H_2O$. F. B.

Preparation of Octendione and its Homologues. FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 227176).—The methylene ketones employed in the following reactions were recently described (Abstr., 1910, i, 652); it is now found that they polymerise readily, yielding octendiones (and higher polymerides) of considerable therapeutic importance.

Δ_α-*Octen-γη-dione*, b. p. 75—76°/21 mm., a colourless oil, sparingly soluble in water, and with a penetrating odour, is prepared by the long boiling of methyleneacetone under reflux, and subsequent fractional distillation of the products: its *semicarbazone* has m. p. 199°.

βζ-Dimethyl-Δ^α*-octen-γη-dione*, $COMe\cdot CHMe\cdot CH_2\cdot CH_2\cdot CO\cdot CMe{:}CH_2$, is prepared in a similar manner from methyl methylene-ethyl ketone, but owing to the higher temperature employed more of the higher polymerides are simultaneously produced; it is a colourless, highly refractive oil, b. p. 187—194° or 83—85°/17 mm., with pine-like odour, immiscible with water, and slowly decomposed by boiling at atmospheric pressure into its progenitors; its *semicarbazone* has m. p. 183°. Dimethyloctendione can also be obtained by the slow distillation in a vacuum of *βζ*-dimethyloctan-*γη*-dione-*α*-ol (see this vol., i, 102) with an equal weight of hydrogen potassium sulphate, or by boiling it with acetic anhydride. F. M. G. M.

The Influence of Inactive Substances on the Rotation of Lævulose. NEUMANN WENDER (*Biochem. Zeitsch.*, 1911, 30, 357—373).—The addition of inorganic acids to a solution of lævulose was found in most cases to increase the specific rotation, the increase varying with the degree of acidity of the solution. Inorganic salts as well as organic acids varied in their behaviour, causing in some cases a rise, in others a decrease, in the rotation. Alcohols and acetone produced a marked diminution in the rotation, which was proportional to the amount added. W. J. Y.

Mercerised Cellulose. CHARLES F. CROSS (*Ber.*, 1911, 44, 153—154).—In connexion with Miller's results (this vol., i, 17) it is pointed out that bleached cotton is not a homogeneous cellulose, and that by the action of sodium hydroxide solution the *β*-celluloses are dissolved. Previous heating at 90—100° renders the *β*-celluloses still more reactive towards alkalis. The increase in weight of the cellulose on hydration is compensated by the loss in weight due to the removal of the *β*-celluloses (compare Cross and Bevan, "Cellulose," pp. 4 and 28).

The author upholds the view that a definite series of hydrated celluloses exists, and that these are stable within the limits 0° to 50°. J. J. S.

Mercerised Cellulose. CARL G. SCHWALBE (*Ber.*, 1911, 44, 151—152. Compare preceding abstract).—Attention is drawn to the

act that during treatment with sodium hydroxide solution a portion of the cellulose is dissolved.

Previous experiments (Abstr., 1908, ii, 627) have shown that mercerised cellulose does not contain water (compare also Ost and Westhoff, Abstr., 1909, i, 210).

According to Liebermann (*Dingler's polyt. J.*, 1886, **181**, 133) an aqueous solution of rosaniline base does not dye cotton-cellulose. For behaviour of mercerised cotton towards substantive dyes, compare Knecht (*J. Soc. Dyers*, 1908, **24**, 68), and Hübner and Pope (*J. Soc. Chem. Ind.*, 1904, **23**, 401).

J. J. S.

Cellulose. II. Hydrocellulose. H. Jentgen (*Zeitsch. angew. Chem.*, 1911, **24**, 11—12. Compare Abstr., 1910, i, 654).—In support of the view that acid in the molecular condition brings about the conversion of cellulose to hydrocellulose (compare Schwalbe, Abstr., 1910, i, 817), the following facts are given: (1) A 1% aqueous acid solution has practically no hydrolysing effect; (2) Methyl or ethyl alcoholic solutions act slowly, and the action depends on the amount of dissociation; (3) 1% solutions of acids in non-ionising media hydrolyse readily. The compounds of cellulose with the molecular acids are regarded as catalysts. The hydrolysis observed by Schwalbe during acetylation is regarded as a secondary or tertiary process.

J. J. S.

Hydrocellulose. Carl G. Schwalbe (*Zeitsch. angew. Chem.*, 1911, **24**, 12—13. Compare Abstr., 1910, i, 817).—Mainly polemical in reply to Jentgen (preceding abstract).

J. J. S.

Acyl Derivatives of Guanidine. Wilhelm Traube (*Ber.*, 1910, **43**, 3586—3590).—Guanidine interacts with the esters of monobasic acids, forming simple acyl guanidines.

Formylguanidine, $NH_2 \cdot C(NH) \cdot NH \cdot CHO$, separates in crystalline granules, m. p. 178° (decomp.). On shaking with bromine, *formylbromoguanidine* results; it crystallises in almost colourless needles, which decompose violently at 125°.

Acetylguanidine separates in colourless, rhombic crystals, m. p. 185° to a clear liquid; on further heating, it solidifies, and the new compound, after crystallisation from water, has m. p. 261°. Acetylguanidine hydrochloride has m. p. 145° (Korndörfer found 142°, *Arch. Pharm.*, 1903, **241**, 449).

Chloroacetylguanidine crystallises in slender, colourless needles, m. p. 125°. *Trichloroacetylguanidine* forms small, colourless crystals, m. p. 183°; the *hydrochloride* crystallises in platelets.

Benzoylguanidine forms short, colourless crystals, m. p. 160°; the hydrochloride separates in lustrous needles, m. p. 207° (Korndörfer found 210°, *loc. cit.*).

m-Nitrobenzoylguanidine crystallises in stellate needles, m. p. 195—197°.

E. F. A.

Complex Salts of Certain Amino-acids. Leo Tschugaeff and F. Serbin (*Compt. rend.*, 1910, **151**, 1361—1363).—α-Amino-acids form stable, complex, internal salts with certain heavy metals, in

this respect differing from the β-, γ-, and δ-acids, which appear unable to do so. The following salts are sparingly soluble, and were prepared in each case by boiling an aqueous solution of the amino-acid with somewhat less than the calculated amount of purpureochromium chloride.

The *glycine* salt, $Cr\left(<\begin{matrix}NH_2\cdot CH_2\\ O-\!\!-CO\end{matrix}\right)_3$, crystallises in small, bright red prisms; it is stable at 300°, and is not decomposed by boiling with alkalis or dilute acids.

The *alanine* salt, $Cr\left(<\begin{matrix}NH_2\cdot CHMe\\ O-\!\!-CO\end{matrix}\right)_3$, has a similar constitution, and shows the same properties; it crystallises in rosy needles. The *asparagine* derivative, $Cr(C_4H_7O_3N_2)_3$, is less soluble, and separates in microscopic, rose-violet needles. α-Amino*iso*butyric acid, α-aminoisovaleric acid, and leucine form similar compounds. The salts can also be prepared, but in a less pure state, by boiling the amino-acids with an aqueous, ammoniacal solution of chromic chloride. When glycine is treated in this way, a basic salt is obtained, for which the constitution $\left(\begin{matrix}CH_2\cdot NH_2\\ CO-\!\!-O\end{matrix}>\right)_2Cr<\begin{matrix}OH\\ OH\end{matrix}>Cr\left(<\begin{matrix}NH_2\cdot CH_2\\ O-\!\!-CO\end{matrix}\right)_2$, is suggested.

W. O. W.

Action of Carbon Disulphide on Amino-acids. Max Siegfried and O. Weidenhaupt (*Zeitsch. physiol. Chem.*, 1910, 70, 152—160).—Carbon disulphide combines with amino-acids in the presence of barium hydroxide or other alkalis in much the same manner that carbon dioxide does (compare Abstr., 1905, ii, 332; 1906, i, 324; 1908, i, 379), yielding dithiocarboxylic derivatives of the amino-acids; for example, glycol yields a salt of

$$CO_2H\cdot CH_2\cdot NH\cdot CS\cdot SH.$$

Most of the salts are readily soluble, but, when treated with benzyl chloride, yield sparingly soluble acid benzyl esters of the type $CO_2H\cdot CH_2\cdot NH\cdot CS\cdot S\cdot CH_2Ph$, by means of which the dithiocarboxylic acids can be isolated with great ease.

Benzyl hydrogen glycinedithiocarboxylate, $C_{10}H_{11}O_2NS_2$, crystallises from water in long, broad, colourless needles with a silvery lustre, and has m. p. 165°; 100 c.c. of an aqueous solution saturated at the ordinary temperature contains 0·0096 gram of ester. The *barium* salt, $(C_{10}H_{10}O_2NS_2)_2Ba$, crystallises from hot water in broad needles.

The yield of ester is 50% when the theoretical amount (2 mols.) of potassium hydroxide (78·6% solution) is used, but falls to nil when 1·5 times the theoretical amount is used.

Benzyl hydrogen dl-*alaninedithiocarboxylate*,

$$CO_2H\cdot CHMe\cdot NH\cdot CS_2\cdot CH_2Ph,$$

crystallises from water in short, colourless, glistening needles, m. p. 36°. Its solubility at 20° is 0·0102.

Benzyl hydrogen phenylglycinedithiocarboxylate,

$$CO_2H\cdot CH_2\cdot NPh\cdot CS_2\cdot CH_2Ph,$$

crystallises from water in slender needles, m. p. 171°. Its solubility

water at 20° is 0·0038, and it is only sparingly soluble in hot water.

The acid *benzyl* ester of *dithiocarboxyphenylaminoacetic acid*, $CO_2H{\cdot}CHPh{\cdot}NH{\cdot}CS_2{\cdot}CH_2Ph$, crystallises from aqueous alcohol in needles, m. p. 88°; the *barium* salt, $(C_{16}H_{14}O_2NS_2)_2Ba$, crystallises in slender needles.

Benzyl hydrogen sarcosinedithiocarboxylate,

$$CO_2H{\cdot}CH_2{\cdot}NMe{\cdot}CS_2{\cdot}CH_2Ph,$$

crystallises from hot water in colourless needles, m. p. 125°, and has solubility 0·0153 at 20°. The *barium* salt forms rhombs. *Benzyl hydrogen asparaginedithiocarboxylate*,

$$CO_2H{\cdot}C_2N_2(CO{\cdot}NH_2){\cdot}NH{\cdot}CS_2{\cdot}CH_2Ph,$$

has m. p. 180°, and yields a *barium* salt, which crystallises in slender needles.

Similar compounds have not been obtained from arginine, lysine, histidine, aspartic acid, and glutamic acid; the leucine derivative is oily.

The formation of the sparingly soluble benzyl ester affords a simple method for the separation of glycine from aspartic or glutamic acids.

J. J. S.

Syntheses of Bases of the Sugar Group. Emil Fischer and Karl Zach (*Ber.*, 1911, **44**, 132—135).—*Aminomethylglucoside hydrobromide*, $C_7H_{15}O_5N,HBr$, is formed when triacetylmethylglucoside bromohydrin (Fischer and Armstrong, Abstr., 1902, i, 263) reacts with ammonia at the ordinary temperature. The acetyl derivative (10 grams) is sealed up with 12—15 c.c. of solid ammonia. The temperature is allowed to rise gradually to the ordinary temperature, at which it is kept for seven days, and the tube then opened after the ammonia has been again solidified. After removal of the excess of ammonia, the syrup is extracted with absolute alcohol, the alcohol evaporated under reduced pressure, and the residue extracted with warm, dry ethyl acetate, which removes acetamide and leaves a mixture of ammonium bromide and the hydrobromide of the amino-glucoside; the latter is obtained from the mixture in a crystalline form by dissolving in a little warm methyl alcohol and adding much ethyl acetate. To remove the last traces of ammonium bromide, the compound is dissolved in absolute alcohol. The yield is 56% of the theoretical. The salt has not a well-defined m. p., but melts and decomposes at about 205° (corr.). It has $[\alpha]_D^{20}$ −21·2°. The *hydrochloride* has m. p. 215° (decomp., corr.) and $[\alpha]_D^{20}$ −25·1°, and both salts dissolve readily in water. The free base dissolves in methyl alcohol, but is precipitated as a flocculent mass on the addition of ether. When heated with *N*-hydrochloric acid in a sealed tube at 100°, the hydrochloride yields the salt of an amino-sugar. This reduces Fehling's solution, but is not identical with glucosamine hydrochloride, since it dissolves more readily in water and concentrated hydrochloric acid, and is decomposed much more readily than glucosamine by concentrated hydrochloric acid. The osazone, which it yields with sodium acetate and phenylhydrazine hydrochloride, is not identical with phenylglucosazone.

J. J. S.

Preparation of Double Compounds of Carbamide with Alkaline-earth Bromides. GEHE & Co. (D.R.-P. 226224).—The action of carbamide on the alkaline-earth bromides yields compounds of therapeutic value in heart complaints.

Calcium bromocarbamide, m. p. 186°, is prepared by heating calcium bromide (250 parts) with carbamide (225 parts) in the presence of a small quantity of alcohol or water during three hours under a reflux condenser; it crystallises from alcohol or ether.

F. M. G. M.

Preparation of Substituted Carbamic Acid Esters. VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 225712).—*α-Methyl-β-trichloroethyl allophanate*, $C_5H_7O_3N_2Cl_3$, prisms, m. p. 186°, is prepared by heating trichloro*iso*propyl alcohol (1 mol.) with carbamic chloride (2 mols.) on the water-bath.

Tetrachloroethyl allophanate, $C_4H_4O_3N_2Cl_4$, is obtained by substituting chloral for the alcohol in the foregoing preparation and allowing the mixture to remain at the ordinary temperature during two days; it forms colourless crystals, which decompose at about 160°. When molecular proportions of trichloro*iso*propyl alcohol and *p*-ethoxyphenylcarbimide are heated together at 185°, *trichloroisopropyl p-ethoxyphenylcarbamate*, $C_{12}H_{14}O_3NCl_3$, is obtained as a syrup, which after crystallisation from petroleum has m. p. 86°. F. M. G. M.

Preparation of Esters of Allophanic Acid. CHEMISCHE WERKE VORM. DR. HEINRICH BYK (D.R.-P. 226228).—Tertiary alcoholic esters which are therapeutically important are not readily prepared by the ordinary methods, and allophanic tertiary alcoholic esters have not previously been obtained.

Amyl allophanate, $CMe_2Et\cdot O\cdot CO\cdot NH\cdot CO\cdot NH_2$, colourless needles, m. p. 149—150°, is prepared by treating a cooled solution of amylene hydrate in an indifferent solvent with cyanic acid and evaporating in a vacuum; it is sparingly soluble in water, ether, or benzene, readily so in alcohol, and is decomposed by hot alkalis. F. M. G. M.

Preparation of α-Bromo-α-ethylbutyrylcarbamide. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 225710).—*α-Bromo-α-ethylbutyrylcarbamide*, $CBrEt_2\cdot CO\cdot NH\cdot CO\cdot NH_2$, colourless, tasteless, odourless crystals, m. p. 114—118°, and of therapeutic value, is prepared (1) by heating α-bromo-α-ethylbutyryl bromide (obtained by the action of bromine on α-ethylbutyric anhydride) with carbamide at 100°; (2) by the action of sulphuric acid on α-bromoethylbutyrylcyanamide (prepared from cyanamide and α-bromoethylbutyryl chloride); (3) from the interaction of ammonium acetate with *phenyl α-bromo-α-ethylbutyrylcarbamate*, which forms colourless crystals, and is prepared from α-bromo-α-ethylbutyryl bromide and the sodium derivative of phenyl carbamate; (4) by the oxidation of α-bromo-α-ethylbutyrylthiocarbamide with potassium permanganate, or (5) the direct bromination of α-ethylbutyrylcarbamide. F. M. G. M.

Calcium Cyanamide. NIKODEM CARO (*Zeitsch. angew. Chem.* 1910, **23**, 2405—2417).—[With B. SCHÜCK]—When solutions contain

ng dicyanodiamide and silver nitrate, in the mol. proportions 1 : 1, : 1, and 3 : 1 are mixed, the compounds $AgNO_3,C_2H_4N_4$, $AgNO_3,2C_2H_4N_4$,

nd $AgNO_3,3C_2H_4N_4$ are produced. The first of these substances is onverted by sodium hydroxide into the compound $C_2H_3N_4Ag$, whilst he second yields a mixture of the same compound and silver oxide.

Silver dicyanodiamide decomposes when boiled, first into silver yanamide; when the boiling is more prolonged, the latter is further ecomposed with production of cyanamide.

Cyanamide, dicyanodiamide, and carbamide are estimated as follows: Calcium cyanamide (7 grams) is shaken for two and a-half hours with 400 c.c. of water, and the solution made up to 500 c.c. A portion of the solution (250 c.c.) is treated with ammonia and silver acetate, diluted to 400 c.c., filtered, and the precipitate washed. The nitrogen (cyanamide) is then estimated by the Kjeldahl method. A part of the filtrate (300 c.c.) is boiled with potassium hydroxide, diluted to 400 c.c., and the nitrogen in the precipitate (dicyanodiamide) estimated as before. A part of the filtrate (300 c.c.) is evaporated down, the silver precipitated with hydrogen sulphide, and the excess of the latter expelled by carbon dioxide. It is then diluted to 400 c.c., and the nitrogen (carbamide) estimated in 100 c.c.

[With Richard Jacoby and B. Schück.]—When calcium carbide is heated in absence of air with 10% sodium cyanide for three hours at 900°, nearly the whole of the cyanide is converted into cyanamide. The same change occurs when barium cyanide is heated in a current of acetylene diluted with hydrogen.

[With B. Schück.]—When calcium cyanamide is heated in a current of dry carbon dioxide, the carbide present is completely decomposed, and the calcium cyanamide is decomposed with production of carbon.

[With R. Jacoby and B. Schück.]—As regards the alleged production of nitrides by the action of nitrogen on a mixture of alumina and carbide, it was found that neither nitrides nor cyanamide are produced at 800—1200°, products being obtained containing not more than 0·8% per cent. N at the lower temperature, and generally no nitrogen at temperatures of 1000° or more. Calcium carbide when heated with alumina in an inert atmosphere yields a black substance containing neither calcium nor aluminium carbide.

[With B. Schück.]—Pure cyanamide can be prepared by slowly adding sodium cyanamide to well cooled, strong hydrochloric acid, and distilling off the water in a vacuum. The cyanamide is then dissolved in ether.

It can also be obtained by adding a concentrated solution of aluminium sulphate to an aqueous extract of calcium cyanamide. The filtrate is distilled in a vacuum and extracted with ether. Cyanamide forms colourless crystals, m. p. 41—42°, readily soluble in water, alcohol, and ether. When heated, it is at once converted into dicyanodiamide (m. p. 204°); the same change takes place when it is exposed to air.

[With R. Jacoby.]—The temperature at which nitrogen acts on mixtures of baryta and carbon is reduced by adding fluorides; the

action takes place at a temperature below the m. p. of the fluoride. When a mixture of barium carbonate, carbon, and calcium (or barium) fluoride is heated without nitrogen at the temperatures employed for nitrogen fixation, there is a production of carbide. No carbide is formed at this temperature in absence of fluoride. N. H. J. M.

Preparation of Phenylnitromethane [ω-Nitrotoluene] by the Action of Mercurous Nitrite on Benzyl Chloride. PASCHÁSAN NEOGI and BIRENDRA BHUSAN ADHICÁRY (*Zeitsch. anorg. Chem.*, 1911, **69**, 270—272).—ω-Nitrotoluene is readily obtained by the interaction of mercurous nitrite and benzyl chloride, the reaction mixture being fractionally distilled under diminished pressure. The yield is much better than when silver nitrite is used. T. S. P.

Preparation of Diphenylmethane and its Homologues. ERNST VON MEYER (*J. pr. Chem.*, 1910, [ii], **82**, 538—540).—The hydrocarbon obtained by the action of phosphoric oxide on benzyl ethyl ether in benzene solution, and regarded by Schickler as an isomeride of stilbene, is shown to be diphenylmethane, not only by the fact that it is not formed when light petroleum is used as the solvent, but also by its oxidation to benzophenone by chromic and acetic acids, and by its nitration to 4 : 4′-dinitrodiphenylmethane and tetranitrodiphenylmethane.

Phenyl-*p*-tolylmethane and phenyl-α-naphthylmethane are obtained in a similar manner by replacing the benzene by toluene and naphthalene respectively; *p*-chlorodiphenylmethane is obtained by using *p*-chlorobenzyl ethyl ether instead of benzyl ethyl ether, and triphenylmethane by employing diphenylmethyl ethyl ether.

C. S.

Triphenylmethyl Chloride, Diphenylcarbamyl Chloride, and Cyanuric Bromide Acting as Acid Halogenides. ERNST VON MEYER (*J. pr. Chem.*, 1910, [ii], **82**, 521—538).—A comparative study of transformations in which triphenylmethyl chloride, diphenylcarbamyl chloride, and cyanuric bromide function as acid halogenides.

[With P. FISCHER.]—Triphenylmethyl chloride reacts with carbamide, methylcarbamide, and phenylcarbamide in pyridine to form *s-ditriphenylmethylcarbamide*, $CO(NH\cdot CPh_3)_2$, *s-triphenylmethylmethylcarbamide*, $NHMe\cdot CO\cdot NH\cdot CPh_3$, m. p. 263°, and *s-phenyltriphenylmethylcarbamide*, $NHPh\cdot CO\cdot NH\cdot CPh_3$, m. p. 242°, respectively, and with thiocarbamide to form *triphenylmethylthiocarbamide*, $NH_2\cdot CS\cdot NH\cdot CPh_3$, m. p. 217°. Triphenylmethyl chloride reacts with potassium phthalimide at 200° to form *triphenylmethylphthalimide*, $C_6H_4<^{CO}_{CO}>N\cdot CPh_3$, m. p. 172°, with pyrrole and with piperidine, yielding *triphenylmethylpyrrole*, $C_4NH_4\cdot CPh_3$, m. p. 258°, and *triphenylmethylpiperidine*, $C_5NH_{10}\cdot CPh_3$, m. p. 153°, respectively, and with pyridine or quinoline in benzene solution readily forms the crystalline additive compounds, C_5NH_5,CPh_3Cl, m. p. 171°, and C_9NH_7,CPh_3Cl, m. p. 163°, which are decomposed by water or alcohol, and form intensely yellow solutions in hot pyridine. When fused with phenol or with resorcinol, triphenylmethyl chloride yields *p*-hydroxytetraphenylmethane and *dihydroxy-*

tetraphenylmethane, $CPh_3{\cdot}C_6H_4(OH)_2$, m. p. 268°, respectively; with mercaptans in benzene or ethereal solution, however, the chloride acts as an acid chloride, yielding thio-ethers: *triphenylmethyl methyl sulphide*, m. p. 105°, from methyl mercaptan, *triphenylmethyl ethyl sulphide*, m. p. 125°, from ethyl mercaptan, and *phenyl triphenylmethyl sulphide*, m. p. 105°, from phenyl mercaptan. Triphenylmethyl chloride reacts with alcoholic *p* toluene-sulphinic acid at 130° to form acetaldehyde and triphenylmethane by the decomposition of the initially formed triphenylmethyl ethyl ether, and yields with sodium *p*-toluenesulphinate, in benzene, *p-tolyltriphenylmethylsulphone*, $CPh_3{\cdot}SO_2{\cdot}C_6H_4Me$, m. p. 173°, which is decomposed by water into triphenylcarbinol and *p*-toluenesulphinic acid. Triphenylmethyl chloride reacts in ether with magnesium benzyl chloride to form *triphenylbenzylmethane*, m. p. 140°, with magnesium *p*-chlorobenzyl chloride to form *triphenyl-p-chlorobenzylmethane*, m. p. 172°, and with magnesium phenyl bromide to form diphenyl and triphenylmethyl, the latter being obtained in the form of its peroxide.

[With A. NICOLAUS.]—Diphenylcarbamyl chloride and pyridine yield an additive compound, $C_5NH_5,NPh_2{\cdot}COCl$, m. p. 107°, which forms a *platinichloride*, decomp. 170°, *picrate*, m. p. 161°, and *iodide*, m. p. 182°. The formation of esters from diphenylcarbamyl chloride and alcohols only occurs very slowly; easily, however, in the presence of a little alkali or potassium cyanide; ethyl diphenylcarbamate has m. p. 72°, the corresponding *methyl* and *isopropyl* esters, 86° and 117° respectively.

Triphenylsemicarbazide (*s-Diphenylcarbamylphenylhydrazide*),

$$NHPh{\cdot}NH{\cdot}CO{\cdot}NPh_2$$

(*acetyl* derivative, m. p. 165°; *nitroso*-compound, m. p. 131°), is obtained readily from phenylhydrazine (2 mols.) and diphenylcarbamyl chloride in benzene, and is oxidised by alcoholic ferric chloride to *diphenylcarbamylazophenyl*, $NPh{:}N{\cdot}CO{\cdot}NPh_2$, m. p. 138°, red needles, which develops a deep red coloration with concentrated sulphuric acid. The interaction of diphenylcarbamyl chloride and aliphatic amino-acids is accomplished best by employing the latter in the form of their esters or sodium salts, acetone being used as solvents; thus *α-diphenylcarbamidopropionic acid*, $CO_2H{\cdot}CHMe{\cdot}NH{\cdot}CO{\cdot}NPh_2$, m. p. 149°, is obtained from alanine, and *α-diphenylcarbamidohexoic acid*,

$$CH_3Me{\cdot}[CH_2]_2{\cdot}CH(CO_2H){\cdot}NH{\cdot}CO{\cdot}NPh_2,$$

m. p. 52°, from leucine.

Ethyl o-*diphenylcarbamidobenzoate*, $CO_2Et{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}NPh_2$, m. p. 108°, obtained by heating equal molecular quantities of ethyl anthranilate and diphenylcarbamyl chloride with an excess of zinc dust at about 100°, yields the free *acid*, m. p. 178°, by hydrolysis. The halogen in diphenylcarbamyl chloride is readily replaced by an alkyl or aryl group by the Grignard reaction; thus with magnesium ethyl iodide it yields *diphenylpropionamide*, m. p. 58°, with magnesium propyl bromide, *diphenylbutyramide*, m. p. 47°, and with magnesium phenyl bromide, *diphenylbenzamide*, m. p. 176°. *Diphenylcarbamyl cyanide*, $NPh_2{\cdot}CO{\cdot}CN$, m. p. 126°, obtained from the chloride and an excess of potassium cyanide at 180—200°, yields diphenylamine, hydrogen cyanide, and carbon dioxide by hydrolysis with alcoholic

potassium hydroxide; it forms an *amido-oxime*, $NPh_2{\cdot}CO{\cdot}C(NH_2){:}NOH$, m. p. 222·5°, with alcoholic hydroxylamine at 60—80°, and is converted in alcoholic solution into the *thioamide*, $NPh_2{\cdot}CO{\cdot}CS{\cdot}NH_2$, m. p. 220°, by hydrogen sulphide in the presence of aqueous ammonia.

[With FRAULEIN NÄBE.]—Cyanuric bromide is obtained in 70—80% yield by the action of nascent hydrogen bromide on a benzene solution of cyanogen bromide. Cyanuric bromide forms cyanuric trihydrazide with 10% hydrazine, cyanuric triphenylhydrazide with ethereal phenylhydrazine, and in boiling benzene reacts (*a*) with *o*-chloroaniline to form *cyanuric tri-o-chloroanilide* (*trichlorophenylmelamine*),

$$(CN)_3(NH{\cdot}C_6H_4Cl)_3,$$

m. p. 161°; (*b*) with 2 : 4-dichloroaniline to form *cyanuric tri-2 : 4-dichloroanilide*, m. p. 261°; (*c*) with *m*-nitroaniline to form *trinitrophenylmelamine*, $(CN)_3(NH{\cdot}C_6H_4{\cdot}NO_2)_3$; (*d*) with α-naphthylamine to form *tri-α-naphthylmelamine*, $(CN)_3(NH{\cdot}C_{10}H_7)_3$, m. p. 225°; (*e*) with methylaniline to form *triphenyltrimethylmelamine*, $(CN)_3(NMePh)_3$, m. p. 115°; (*f*) with benzylaniline to form *triphenyltribenzylmelamine*, m. p. 120°; (*g*) with *p*-aminophenol to form *cyanuric di-p-hydroxycyanilide bromide*, $(CN)_3(NH{\cdot}C_6H_4{\cdot}OH)_2Br$, m. p. 275° (decomp.); (*h*) with *p*-anisidine to form a corresponding *anisidide*,

$$(CN)_3(NH{\cdot}C_6H_4{\cdot}OMe)_2Br,$$

m. p. 250° (decomp.), and (*i*) with anthranilic acid to form the *substance*, $(CN)_3(NH{\cdot}C_6H_4{\cdot}CO_2H)_2Br$, m. p. 197°. Cyanuric bromide and carbamide (3 mols.) at 130—140° yield *tricarbamylmelamine*,

$$(CN)_3(NH{\cdot}CO{\cdot}NH_2)_3,$$

m. p. above 300°.

Cyanuric bromide reacts in the normal way with aluminium chloride and an aromatic hydrocarbon in the presence of carbon disulphide, forming substances of the type: $(CN)_3Ar_3$; Ar = Ph, m. p. 231°; Ar = *p*-C_6H_4Me, m. p. 275—276°; Ar = 3 : 4-$C_6H_3Me_2$, m. p. 210°; Ar = 2 : 4-$C_6H_3Me_2$, m. p. 155°; Ar = *p*-$C_6H_4{\cdot}OMe$, m. p. 115°; Ar = α-$C_{10}H_7$, m. p. 190—200°; the constitutions of these compounds (excluding the first) are determined by the fact that hydrolysis by hydrochloric acid at 200—220° yields *p*-toluic, 3 : 4-dimethylbenzoic, 2 : 4-dimethylbenzoic, anisic, and α-naphthoic acids respectively. The analogous triethyl compound, $(CN)_3Et_3$, obtained by Otto and Voigt from dichloropropionitrile is also produced by the interaction of cyanuric bromide and ethereal magnesium ethyl iodide. C. S.

Triarylmethyls. V. WILHELM SCHLENK and ANNA HERZENSTEIN (*Ber.*, 1910, **43**, 3541—3546. Compare Abstr., 1909, *i*, 791; 1910, *i*, 236, 237, 469).—According to the authors, the sole objection to the hexaphenylethane formula for the colourless form of triphenylmethyl lies in the comparative stability of the closely related pentaphenylethane. Investigation of the behaviour of the latter compound in high boiling solvents shows, however, that the remarkable power of dissociation characteristic of "colourless" triphenylmethyl is also shared by pentaphenylethane, although in a less marked degree.

Solutions of pentaphenylethane in anisole or ethyl benzoate, on being heated rapidly to boiling, acquire the deep yellowish-brown colour of a hot solution of triphenylmethyl; on quickly cooling, the colour

diminishes to a light yellow. The solution decolorises iodine, and at once becomes colourless when shaken with air; the colour, however, rapidly reappears, and finally vanishes only by repeated shaking with air. This behaviour so closely resembles that of triphenylmethyl solutions that there can be no doubt that triphenylmethyl is one of the products of dissociation of pentaphenylethane, $Ph_3C{-}CHPh_2$. The second dissociation product, diphenylmethyl, polymerises to tetraphenylethane, which can be readily isolated by boiling pentaphenylethane in ethyl benzoate solution in an atmosphere of nitrogen.

On passing oxygen through a boiling solution of pentaphenylethane in ethyl benzoate, the diphenylmethyl is oxidised to tetraphenylethylene.

A new method of formation of hexa-arylethanes is also described. When a concentrated benzene solution of molecular quantities of 4-phenyl-triphenylmethane and 4-phenyl-triphenylmethyl chloride is exposed to sunlight, it acquires a reddish colour, due to the formation of 4-phenyl-triphenylmethyl: $C_6H_4Ph{\cdot}CPh_2H + ClCPh_2{\cdot}C_6H_4Ph \rightleftharpoons C_6H_4Ph{\cdot}CPh_2\cdots CPh_2{\cdot}C_6H_4Ph + HCl$.

The reaction is, however, reversible, the amount of 4-phenyl-triphenylmethyl being very small when equilibrium is attained.

In a similar manner phenylbisdiphenylmethyl, $CPh(C_6H_4Ph)_2$, is obtained from phenylbisdiphenylmethane and phenylbisdiphenylmethyl chloride.

Diphenylbisdiphenylene-ethane, $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!>\!CPh{\cdot}CPh<\!\begin{matrix}C_6H_4\\C_6H_4\end{matrix}$, on account of its stability towards hydrochloric acid, is produced in quantitative yield by exposing a concentrated benzene solution of phenyldiphenylenemethyl chloride and phenyldiphenylenemethane (phenylfluorene) to the action of sunlight. F. B.

Hydrogenations in Presence of Palladium. Applications to Phenanthrene. Pierre Breteau (*Compt. rend.*, 1910, 151, 1368—1369).—By passing a mixture of phenanthrene vapour and hydrogen over spongy palladium at 160°, a mixture of the tetra- and octa-hydride is obtained; when hydrogenation is carried out at the ordinary temperature, in presence of palladium black suspended in *cyclo*hexane, only the tetrahydride is formed. Precipitated palladium, prepared by treating a solution of the chloride in hydrochloric acid with zinc, also yields the tetrahydride when brought into contact with phenanthrene in alcoholic solution. W. O. W.

Action of Concentrated Sulphuric Acid on Some Aromatic Nitroamines. II. Derivatives of Methylaniline. Methyl-*p*-anisidine, and Methyltoluidines. Frédéric Reverdin (*Bull. Soc. chim.*, 1911, [iv], 9, 43—49. Compare Abstr., 1910, i, 255).—Further instances are given of the reduction of the nitro- to the nitroso-group by sulphuric acid in certain aromatic nitro-derivatives, and it is shown that this reaction explains why such nitro-derivatives respond to Liebermann's test.

2 : 4 : 6-Trinitrophenylmethylnitroamine, on treatment with sulphuric acid at atmospheric temperature, furnishes picramide and some nitrosomethylpicramide (Bamberger and Müller, Abstr., 1900, i, 217). The latter is also produced if alcohol is used along with sulphuric acid,

but in this case the principal product of the reaction is trinitromethylaniline.

Dimethyl-*p*-anisidine, on nitration in the cold, furnishes the N-*nitroso*-derivative of dinitromethyl-*p*-anisidine, m. p. 111—112°, but with hot nitric acid gives the N-*nitro*-derivative, m. p. 125°, which may also be obtained by the further action of nitric acid on the nitrosoamine, and, conversely, the latter is reproduced by the action of sulphuric acid on the nitroamine. Further, when the nitroamine is heated with phenol or the nitrosoamine is heated with hydrochloric acid, *dinitromethyl*-p-*anisidine*, m. p. 129°, is formed. By boiling the nitroamine with sodium hydroxide solution, a small yield of Weselsky and Benedikt's dinitroquinol methyl ether (Abstr., 1881, 1139) is obtained. The fact that this nitroamine, like that obtained from dimethyl-*o*-anisidine (Abstr., 1910, i, 255), gave the Liebermann reaction, led the author to examine nitroamines obtained from alkyltoluidines, and for this purpose 3 : 5-dinitro-*o*-tolylmethylnitroamine and its *p*-isomeride were prepared by the method described by van Romburgh (*Rec. trav. chim.*, 1884, 3, 392). As secondary products in these preparations some 3 : 5-dinitro-2-nitromethylaminobenzoic acid and its 4-isomeride were obtained (Abstr., 1908, i, 167). These melted at 187° and 204° respectively. Both nitroamines gave Liebermann's reaction. The first on treatment with sulphuric acid at atmospheric temperature gives Stoermer's 3 : 5-dinitro-*o*-tolylmethylnitrosoamine (Abstr., 1899, i, 44), but is recovered unchanged from sulphuric acid at −10°. 3 : 5-Dinitro-*o*-tolylmethylnitroamine, with sulphuric acid at atmospheric temperature, furnishes 3 : 5-dinitro-2-nitromethylaminobenzoic acid (see above) and a *substance* crystallising in colourless needles and decomposing above 300°, but with sulphuric acid at −10° it gives the same acid with, as chief product, 3 : 5-dinitro-*p*-tolylmethylnitrosoamine, m. p. 127—128° (compare van Romburgh, Abstr., 1896, i, 478). T. A. H.

The Reaction of Cellulose Nitrate with Dimethylaniline. Johann Walter (*Zeitsch. ang-w. Chem.*, 1911, 24, 62—64).—Gun-cotton and celluloid absorb dimethylaniline, the colour gradually deepening through green and blue to violet. The coloration becomes darker on exposure to light, and is not removed by solvents. Strongly-coloured specimens have an odour of phenylmethylnitrosoamine. Other aromatic amines produce similar colorations, but less rapidly and of less intensity. C. H. D.

Velocities of Addition of Bromine to the Imides of Some Substituted Maleinamic Acids. II. Arnaldo Piutti and G. Calcagni (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1910, [iii], 16, 255—261. Compare Abstr., 1909, i, 360).—Continuing their investigations on this subject, the authors have measured the velocities of addition of bromine to the following imides (compare Abstr., 1910, i, 672): hydroxyphenylmaleinimide (white form), methoxyphenylmaleinimide (white and yellow forms), ethoxyphenylmaleinimide (white and yellow forms). The velocity is very slow in all these cases; for the white imides, the reaction is complete in about fifty days, for the yellow forms in about seventy-five days. Since Bauer has shown that

substance of this type the power of adding on bromine diminishes with increase in the number of negative groups, this forms an additional argument for assigning to the yellow form the symmetrical formula $\begin{matrix}CH\cdot CO\\ \|\\ CH\cdot CO\end{matrix}\!\!>\!N\cdot C_6H_4\cdot OR$. The white isomerides behave as weak bases, and that is consonant with their having the constitution $\begin{matrix}CO\!-\!O\\ |\\ CH\!:\!CH\end{matrix}\!\!>\!C\!:\!N\cdot C_6H_4\cdot OR$. R. V. S.

Preparation of Alkali and Ammonium Salts of Nitrosoarylhydroxylamines. OSKAR BAUDISCH (D.R.-P. 227659).—Nitrosoarylhydroxylamines are known, but their salts have not previously been obtained; they are now prepared by either the oxidation of an amine or the reduction of a nitro-compound in alkaline solution in the presence of sodium nitrite, or an alkyl nitrite.

Ammonium nitrosophenylhydroxylamine, prepared from nitrobenzene, concentrated ammonium hydroxide, zinc dust, and amyl nitrite, crystallises in silvery leaflets, m. p. 163—164°, and sublimes readily.

The *sodium* salt, $C_6H_5\cdot N(NO)\cdot ONa$, and the *potassium* salt form snow-white needles; the *iron* salt crystallises in garnet-red needles or rosettes, with a blue, metallic lustre; it is insoluble in water, but soluble in the ordinary organic solvents; the *copper* salt forms dark grey crystals, and has similar properties. *Ammonium α-nitrosonaphthylhydroxylamine*, colourless leaflets, is rather unstable, turning pink in the light; it dissolves in water, and is converted on boiling into α-nitrosonaphthalene; the *sodium* and *potassium* salts are colourless; the *copper* salt, $(C_{10}H_7O_2N_2)_2Cu$, forms glistening, bluish-grey needles insoluble in water.

The formation of complex double salts of ammonium with copper, nickel, cobalt, or iron is also discussed. F. M. G. M.

Separation of *p*- and *m*-Nitro-*o*-anisidine. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 228357).—The nitration of aceto-*o*-anisidide yields a mixture of two isomeric nitroaceto-*o*-anisidides; these have previously been separated by the more ready hydrolytic dissociation of *p*-nitro-*o*-anisidine, which is precipitated by the addition of water to an acid solution of the mixed sulphates, whilst *m*-nitro-*o*-anisidine sulphate remains in solution.

It is now found that a separation can be effected by fractional crystallisation of the mixed sulphates; the mixture of *m*- and *p*-nitroaceto-*o*-anisidides is hydrolysed by heating with 70% sulphuric acid, and the mixture then diluted with hot water until the concentration of the sulphuric acid is reduced to 40%; on cooling, pure *p-nitro-o-anisidine sulphate* separates in colourless crystals, and the *m*-nitro-*o*-anisidine is precipitated from the filtrate by the addition of alkali.

F. M. G. M.

Preparation of Phenyl Ortho-oxalates. SCHÜLKE and MAYR (D.R.-P. 226231).—When dehydrated oxalic acid is mixed with fused

phenol (2 mols.) at a temperature of about 40°, and then heated to 90—100° with continual stirring, pure *diphenyl ortho-oxalate*,

$$OPh\cdot C(OH)_2\cdot C(OH)_2\cdot OPh,$$

is obtained in quantitative yield; it crystallises from acetic acid, and has m. p. 126°. F. M. G. M.

Synthesis of Alcohols in the *cyclo*Hexane Series. ALPHONSE MAILHE and MARCEL MURAT (*Bull. Soc. chim.*, 1910, [iv], 7, 1083—1089).—The condensation of 1-methyl*cyclo*hexan-3-one with various magnesium alkyl haloids has been studied, and the alcohols obtained, and some of their derivatives are described (compare Sabatier and Mailhe, Abstr., 1906, i, 254; Murat, Abstr., 1909, i, 146).

1-Methyl-3-ethyl*cyclo*hexan-3-ol, D^0 0·9201, D^{20} 0·9013, n_D 1·459, b. p. 88°/20 mm., obtained by condensing 1-methyl*cyclo*hexan-3-one (Abstr., 1905, i, 275) with ethyl magnesium bromide, is a colourless liquid, with a feebly camphoraceous odour (compare Zelinsky, Abstr., 1901, i, 661); the *phenylurethane*, m. p. 98°, crystallises in colourless prisms; the *acetate*, D^0 0·9493, D^{20} 0·9303, n_D 1·441, b. p. 98—100°/20 mm., has a fruity odour. The alcohol is readily dehydrated, yielding 1-*methyl*-3-*ethyl*cyclo*hexene*, D^0 0·8366, D^{20} 0·8296, n_D 1·454, b. p. 149—151°/760 mm., a mobile, colourless liquid of pleasant odour; it gives a greenish coloration with sulphuric acid and alcohol, furnishes a *nitrosochloride*, m. p. 124—126°, and on reduction yields 1-*methyl*-3-*ethyl*cyclo*hexane*, D^0 0·8320, D^{20} 0·8213, n_D 1·460, b. p. 145—146°. 1-Methyl-3-propyl*cyclo*hexan-3-ol, D^0 0·9063, D^{15} 0·8961, n_D 1·461, b. p. 96—98°/20 mm., is a colourless, viscous liquid (Zelinsky, *loc. cit.*); it yields a *phenylurethane*, m. p. 112°, and an *acetate*, D^0 0·9367, D^{20} 0·9248, n_D 1·454, and b. p. 108—110°/20 mm., which is colourless and has a fruity odour. The alcohol is readily dehydrated, yielding 1-*methyl*-3-*propyl*cyclo*hexene*, D^0 0·8375, D^{15} 0·8302, n_D 1·456, and b. p. 168—171°/760 mm., which absorbs bromine and gives a yellowish-green colour with alcohol and sulphuric acid, furnishes a *nitrosochloride*, m. p. 128—131° (decomp.), and on reduction gives 1-*methyl*-3-*propyl*cyclo*hexane*, b. p. 164—165°.

1-*Methyl*-3-iso*butyl*cyclo*hexan*-3-*ol*, D^0 0·9011, D^{19} 0·8972, n_D 1·465, b. p. 107—109°/20 mm., is best obtained by condensing magnesium *iso*butyl chloride with methyl*cyclo*hexanone, although the secondary reaction already described (Abstr., 1905, i, 706) occurs and occasions some loss. The alcohol is viscous and dehydrates easily, giving an *ethylenic hydrocarbon*, b. p. 192—195°, having a somewhat alliaceous odour.

1-*Methyl*-3-iso*amyl*cyclo*hexan*-3-*ol*, D^0 0·8982, D^{22} 0·8856, n_D 1·464, b. p. 126—127°/20 mm., is a viscous, colourless, pleasant-smelling liquid; the *phenylurethane*, m. p. 128°, is crystalline, and the *acetate*, D^{20} 0·9146, n_D 1·457, b. p. 140°/20 mm., is a thick liquid with a pleasant odour. The alcohol on dehydration gives 1-*methyl*-3-iso*amyl*cyclo*hexene*, D^0 0·8301, D^{20} 0·8190, n_D 1·459, b. p. 209—211°/760 mm., which gives a greenish coloration with sulphuric acid and alcohol, yields a *nitrosochloride*, m. p. 136°, and on reduction furnishes 1-*methyl*-3-iso*amyl*cyclo*hexane*, b. p. 205°, a colourless liquid with an odour [illegible]ing that of petrol.

3-cyclo*Hexyl*-1-*methyl*cyclo*hexan*-3-*ol*, D^0 0·9815, D^{18} 0·9685, n_D 1·495, b. p. 153—155°/20 mm., is a viscous liquid of agreeable aroma, yields a *phenylurethane*, m. p. 141°, gives an intense blue coloration with bromine in chloroform, and on dehydration furnishes 3-cyclo*hexyl*-1-*methyl*cyclo*hexene*, D^0 0·9634, D^{18} 0·9138, n_D 1·492, b. p. 240°/760 mm., a mobile liquid which is scarcely coloured by sulphuric acid and alcohol, but gives a *nitrosochloride*, m. p. 142—146°, which is possibly a mixture of isomerides.

3-*Phenyl*-1-*methyl*cyclo*hexan*-3-*ol*, m. p. 61°, b. p. 153°/20 mm. (decomp.), crystallises in monoclinic prisms, yields a *phenylurethane*, m. p. 143°, and on dehydration furnishes 3-*phenyl*-1-*methyl*cyclo*hexene*, D^0 0·9859, D^{20} 0·9702, n_D^{20} 1·555, and b. p. 145°/20 mm., as a colourless, mobile liquid, which absorbs bromine, and with sulphuric acid and alcohol gives a rose-red coloration.

3-*Benzyl*-1-*methyl*cyclo*hexan*-3-*ol*, D^0 1·0032, D^{17} 0·9873, n_D 1·532, b. p. 165°/18 mm. (decomp.), is a colourless liquid, having a lemon-like odour, and is obtained in small yields by condensing methyl*cyclo*hexanone with benzyl magnesium chloride, the chief product being dibenzyl. 3-*Benzyl*-1-*methyl*cyclo*hexene*, D^0 0·9695, D^{20} 0·9591, n_D 1·547, b. p. 156°/20 mm. or 271°/760 mm., is colourless, and has a disagreeable odour. T. A. H.

A Solid Molecular Compound of Hexamethylenetetramine and Guaiacol. F. Hoffmann-La Roche & Co. (D.R.-P. 225924).—The preparation of a hexamethylenetetraminetriguaiacol has been previously described (Abstr., 1910, i, 378). A compound obtained in a similar manner and with identical properties is now found to have the composition of a hexamethylenetetraminediguaiacol, and it is suggested that the former compound was possibly not an individual substance. F. M. G. M.

Fermentation of Tyrosine to *p*-Hydroxyphenylethanol (Tyrosol). Felix Ehrlich (*Ber.*, 1911, *44*, 139—146. Compare Abstr., 1907, ii, 384).—A 60—80% yield of *p*-hydroxyphenylethanol, $OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, can be obtained by the fermentation of tyrosine with large amounts of yeast in the presence of much sugar and of nutritive salts. Small amounts of acids are also formed; these are soluble in ether, and give Millon's reaction. The hydroxy-alcohol is termed *tyrosol*. It crystallises in long, glistening needles and rods of rhombic habit; it has m. p. 93° and b. p. 310°. It has a bitter taste, does not reduce Fehling's solution, and gives a Bordeaux-red coloration when warmed with concentrated sulphuric acid. With ferric chloride solution it gives an indigo-blue coloration, and with Millon's reagent, and also with diazobenzenesulphonic acid, dark red colorations. It does not give the Piria reaction, but develops an intense yellowish-green coloration with formaldehyde and sulphuric acid. It is oxidised by alkaline permanganate solutions, reacts with phosphorus pentachloride, yielding a yellow oil, and also forms an oily acetyl derivative. The *dibenzoyl* derivative, $C_{32}H_{18}O_4$, prepared by the Schotten-Baumann method, crystallises from alcohol in felted needles, m. p. 111°.

The formation of tyrosol is brought about by either top or bottom

yeasts. It is also formed in appreciable amounts when a sterilised solution of tyrosine and sugar is inoculated with pure cultures of yeast, and in small amounts during the fermentation of pure sugar solutions by pure yeasts. Its formation in the latter case is due to the autolysis of the dead yeast cells and the formation of tyrosine, which is used as nitrogenous nutritive material by the living cells and transformed into tyrosol. It is not formed in the absence of sugars.

Tyrosol thus appears to be a by-product in most processes of fermentation by yeast, and is present in all fermented liquors, especially in beer and wine, the flavours of which are due, in part, to the presence of the hydroxy-alcohol. J. J. S.

Preparation of Nitrobenzoic Acids from the Corresponding Nitrotoluenes. Gustav Lüttgen (D.R.-P. 226225).—The oxidation of nitrotoluenes to the corresponding nitrobenzoic acids with nitric and sulphuric acids is not satisfactory; it is now found that the reaction proceeds smoothly in nitric acid solution with potassium chlorate as the oxidising agent. 2 : 4 : 6-Trinitrotoluene was dissolved in concentrated nitric acid (48 Bé), and warmed to 90—95°; potassium chlorate (2 parts) was gradually stirred in, the temperature being maintained meanwhile at 100—120°; pure trinitrobenzoic acid separated from the reaction mixture on cooling. F. M. G. M.

Synthesis of Compounds of the Normal Amyl Series from Piperidine. Julius von Braun and W. Sobecki (*Ber.*, 1910, 43, 3596—3599).—Although benzo-ε-chloroamylamide, derived from piperidine, is very stable, the corresponding benzoiodoamylamide is relatively easily reduced. It is prepared from the chloro-compound by boiling this with sodium iodide in alcohol, and is dissolved in much concentrated hydrochloric and acetic acid, cooled, and stirred with zinc dust for a number of hours.

Benzo-n-amylamide separates as an oil, and is purified by distillation; b. p. 208—210°/15 mm. It is readily hydrolysed to *n*-amylamine, or when distilled with phosphorus pentachloride or pentabromide is converted into *n*-amyl chloride or bromide respectively. To prove that the normal carbon-chain structure had remained intact, the bromide was boiled with potassium cyanide and converted into the nitrile of *n*-hexoic acid. E. F. A.

Secondary Anthranilic Acids and the Transformation of their Nitroso-derivatives into a Peculiar Class of Intensely Red Substances, Soluble in Water. Josef Houben and Th. Arendt (*Ber.*, 1910, 43, 3533—3541. Compare Abstr., 1908, i, 27; 1909, i, 645, 794).—Previous attempts to nitrosylate methyl dimethylanthranilate failed. The authors now find that the action of sodium nitrite and fuming hydrochloric acid on the ester yields 5-nitroso-*N*-methylanthranilic acid, one of the methyl groups being split off from the nitrogen atom.

When 5-nitroso-*N*-methylanthranilic acid is dissolved in sodium carbonate and shaken with acetic anhydride, a red substance is formed,

which is very soluble in water. Similar red products have been obtained by the action of various acid chlorides and anhydrides, either in aqueous or pyridine solution, on a large number of nitroso-derivatives of secondary anthranilic acids and their esters, and also on quinoneoximecarboxylic acid, but only in one instance has the product been isolated.

When 5-nitroso-*N*-methylanthranilic acid is shaken with pyridine and acetic anhydride, a red solution is formed, from which, by the addition of ether, a brownish-red *pyridine* salt, $C_{15}H_{15}O_4N_3$, is precipitated; the salt is very soluble in water, forming blood-red solutions, and melts with decomposition to a dark red liquid.

[With L. ETTINGER.]—N-*Acetonylanthranilic acid*,

$$CO_2H\cdot C_6H_4\cdot NH\cdot CH_2\cdot COMe,$$

prepared by dissolving anthranilic acid in the equivalent quantity of potassium carbonate and boiling the solution with chloroacetone, has m. p. 169—170°; the *nitrosamine*, which forms white crystals, m. p. 115—116° (decomp.), could not be transformed into 5-nitroso-*N*-acetonylanthranilic acid by the action of hydrochloric acid; the *semicarbazone*, $CO_2H\cdot C_6H_4\cdot NH\cdot CH_2\cdot CMe:N\cdot NH\cdot CO\cdot NH_2$, obtained from the *sodium bisulphite* compound of acetonylanthranilic acid, has m. p. 240—241° (decomp.).

Methylacetonylanthranilic acid, $CO_2H\cdot C_6H_4\cdot NMe\cdot CH_2\cdot COMe$, prepared from methylanthranilic acid and chloroacetone, crystallises in small, light grey needles, m. p. 123—126°.

2 : 4-*Dinitrodiphenylmethylamine-2'-carboxylic acid*,

$$CO_2H\cdot C_6H_4\cdot NMe\cdot C_6H_3(NO_2)_2,$$

is obtained by boiling 4-chloro-1 : 3-dinitrobenzene with methylanthranilic acid in aqueous potassium carbonate; it forms clusters of yellow needles, m. p. 178°. F. B.

Action of Ethereal Salts on the Monosodium Derivative of Phenylacetonitrile. F. BODROUX (*Compt. rend.*, 1910, **151**, 1357—1359. Compare Abstr., 1910, i, 623).—Ethyl benzoate condenses with the sodium derivative of phenylacetonitrile to give a 75% yield of cyanophenylacetophenone, $CN\cdot CHPh\cdot COPh$, lamellæ, m. p. 93—94° (compare Walther and Schickler, Abstr., 1897, i, 522). Ethyl carbonate in the same way forms ethyl cyanophenylacetate, $CN\cdot CHPh\cdot CO_2Et$, b. p. 163—165°/19 mm., D^{17} 1·085, the yield being 55%. Ethyl oxalate yields a small quantity of ethyl cyanophenylpyruvate. The foregoing cyano-derivatives are sufficiently acidic to be capable of titration, using phenolphthalein as indicator. W. O. W.

Crystallographic Examination of Some Nitrophenylmethylacrylic Derivatives. FRANCESCO RANFALDI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1910. [iii], **16**, 225—234).—*β-o*-Nitrophenyl-α-methylacrylic acid, $NO_2\cdot C_6H_4\cdot CH:CMe\cdot CO_2H$, forms monoclinic, prismatic crystals [$a:b:c=1·3446:1:1·4562$; $\beta=92°24'51''$]. *β-m*-Nitrophenyl-α-methylacrylic acid forms colourless, acicular crystals, which could not be obtained in a measurable form. *β-p*-Nitrophenyl-α-methylacrylic acid forms triclinic, pinacoidal crystals [$a:b:c=1·2867:1:1·4602$; $\alpha=84°42'8''$; $\beta=83°31'31''$, $\gamma=87°35'18''$]. Sodium *β-o*-nitrophenyl-

α-methylacrylate forms rhombic, disphenoidal crystals [$a:b:c$ = 1·3940 : 1 : 2·0544]. R. V. S.

Preparation of Glycol Monosalicylate. C. F. Boehringer & Söhne (D.R.-P. 225984. Compare Abstr., 1908, i, 176).—The esterification of salicylic acid with ethylene chlorohydrin yields *β-chloroethyl salicylate*, $OH\cdot C_6H_4\cdot CO_2\cdot CH_2\cdot CH_2Cl$, which on careful hydrolysis with mild reagents gives the therapeutically valuable *glycol salicylate*, $OH\cdot C_6H_4\cdot CO_2\cdot CH_2\cdot CH_2\cdot OH$.

The hydrolytic agents described as suitable are (1) sodium acetate and dilute acetic acid; (2) disodium phosphate and water, or (3) sodium salicylate and water, a sealed tube being employed and a temperature of 130° maintained in each case. F. M. G. M.

Pyrogenetic Decomposition of *cyclo*Gallipharic Acid. Hermann Kunz-Krause and Paul Manicke (*Arch. Pharm.*, 1910, 248, 695—709. Compare Abstr., 1904, i, 587; 1910, i, 458, 677).—The decomposition of *cyclo*gallipharic acid when heated alone or with various dehydrating agents has been studied, and the results correlated with those recorded in previous papers (*loc. cit.*).

When heated with potassium hydrogen sulphate, the acid furnishes unsaturated gaseous hydrocarbons, acraldehyde, *cyclo*gallipharol, and 4-hydroxy-*m*-xylene.

Sulphuric acid is without action on *cyclo*gallipharic acid in the cold, but on heating with this reagent, it is converted into the keto-anhydride of *cyclo*gallipharic acid at 125—130°; at 150—160° some *cyclo*gallipharol is formed, and at 180° this substance is the sole product of the reaction.

When heated alone, the temperature being gradually raised from 130° to 250°, the amounts of carbon dioxide evolved indicate that the acid undergoes the same progressive decomposition as with sulphuric acid, the same stages, however, being reached at somewhat higher temperatures. Above 250° complete decomposition into carbon dioxide and volatile hydrocarbons takes place. In conclusion, a summary of the results recorded in this and the two preceding papers of the series is given. T. A. H.

Preparation of Carvacrolphthalein. Curt Ehrlich (D.R.-P. 225983).—*Carvacrolphthalein*, colourless, transparent needles, m. p. 246—247°, is prepared by heating phthalic anhydride (1 part) with carvacrol (2 parts) and stannic chloride (2 parts) at 100° during two hours. It is insoluble in water, soluble in sodium hydroxide with a deep blue colour, and compares very favourably with phenolphthalein as an indicator. F. M. G. M.

Esterification of Unsymmetrical Di- and Poly-basic Acids. XXIII. Trimellitic Acid. Rudolf Wegscheider, Heinrich Felix Perndanner, and Otto Auspitzer (*Monatsh.*, 1910, 31, 1253—1301).—The formation of acid esters of trimellitic acid (benzene-1 : 2 : 4-tricarboxylic acid) by different methods has been studied in order to determine whether the rules previously laid down for dibasic acids

hold good. The investigation was complicated by the fact that the three carboxyl groups differ but little from one another, and therefore mixtures of acid esters are obtained by each method; these mixtures cannot be separated readily into their constituents. They do not crystallise well, and several of them tend to form mixed crystals. The 1 : 4- and 2 : 4-dimethyl esters crystallise extremely slowly, and are usually obtained as syrups, although from their constitutions their m. p.'s should be relatively high. The constitution of the 4-methyl ester,

$$CO_2Me\cdot C_6H_3\cdot(CO_2H)_2\ [(CO_2H)_2:CO_2Me = 1:2:4],$$

follows from the fact that it is formed by the addition of water to the methyl ester of the anhydro-acid, $CO_2Me\cdot C_6H_3:(CO)_2O$, and the constitutions of the two isomeric monomethyl-esters were determined by conversion into the corresponding amidedicarboxylic acid and then by means of bromine and potassium hydroxide, transforming the amides into amino*iso*- and aminotere-phthalic acids. The constitution of the dimethyl esters was determined by the elimination of carbon dioxide from their potassium salts in the presence of lime.

The products formed by the esterification of the acid, both by the direct and by the catalytic method, could not be obtained pure, with the exception of small amounts of the 1- and 2-monomethyl esters, but the fact that the syrups obtained yield appreciable amounts of the methyl ester of anhydrotrimellitic acid points to the conclusion that by these methods the carboxyl groups in position 4, that is, the carboxyl group least affected by "steric hindrance," is first esterified. The 1- and 2-monomethyl esters, under similar conditions, yield the 1 : 4- and 2 : 4-dimethyl esters, and but *little* 1 : 2-dimethyl ester. By partial hydrolysis of the normal ester with potassium hydroxide, the 1 : 2-dimethyl ester is first formed, and, by further hydrolysis, the 2-monomethyl ester, with smaller amounts of the isomeric 1-ester. By the addition of methyl alcohol to the acid anhydride, both the 1- and 2-monomethyl esters are formed, but, at the same time, the carboxylic group in position 4 is esterified to a slight extent. The mono-silver salt with methyl iodide yields mainly 1-methyl, together with the 2-methyl ester, and the disilver salt yields mainly 1 : 2-dimethyl ester. These results agree on the whole with the generalisation that in the formation of acid esters from the acid by esterification, or from neutral esters by hydrolysis, steric hindrance is the determining factor, whereas in the formation from the anhydride or from the acid metallic salts, the relative strengths of the carboxyl groups are of first importance.

Full details of the methods used for separating the mixtures obtained in each experiment are given.

Methyl hydrogen *iso*phthalate has m. p. 167—169°, and not 126° as stated by Meyer (*Monatsh.*, 1901, **22**, 437).

A 20% yield of trimellitic acid can be obtained by the action of nitric acid on French colophony (compare Schoder, *Ann. Chem. Pharm.*, 1874, **172**, 94), provided the mother liquors are worked up. It has not been found possible to prepare the acid from naphthol yellow-*S* by Rée's method (Trans., 1886, **49**, 510), but Schultz' method (Abstr., 1909, i, 897) gives fairly good yields if the chromic anhydride is added

gradually. The m. p. depends on the method of heating; when dipped into a bath at 200°, it has m. p. 215—217° in an open tube or 229—234° in a closed tube. A 2% solution of the normal ammonium salt gives precipitates with solutions of mercuric, cadmium, lead, ferric, aluminium, uranyl, and silver salts.

The following acid salts have been prepared: $CO_2H{\cdot}C_6H_3(CO_2Ag)_2$, slender needles from hot water; $CO_2Ag{\cdot}C_6H_3(CO_2H)_2$; $C_9H_4O_6Ba,H_2O$, insoluble in water.

The 1-*monomethyl* ester, $C_{10}H_8O_6$, is most readily prepared from the mono-silver salt, and is most conveniently separated from the free acid by precipitating the latter in the form of its barium salt; it may be purified by the addition of benzene to its ethereal solution, and has m. p. 203·5—205·5°, but frequently melts to a certain extent at 177°, resolidifies at 179°, and then melts at the higher temperature given. The two m. p.'s are probably due to dimorphism. When mixed with the isomeric 2-*monomethyl* ester, its m. p. is not appreciably affected. The latter ester is best prepared by the partial hydrolysis of the 1 : 2-dimethyl ester; it is sparingly soluble in water, whereas the 1-ester dissolves readily, and crystallises from this medium as a colourless powder, m. p. 208°. The 4-methyl ester is most readily obtained by the addition of water to the methyl ester of the anhydro-acid, and crystallises from water in compact plates, m. p. 145—147°. The *anhydro*-ester, $CO_2Me{\cdot}C_6H_3\langle{}^{CO}_{CO}\rangle O$, has m. p. 94—99°, is transformed into a syrup by the addition of a little alcohol, and when kept for some time, even in a desiccator, yields the 4-monomethyl ester. The 1 : 2-*dimethyl* ester, $C_{11}H_{10}O_6$, crystallises from carbon tetrachloride, or better from a mixture of ether and light petroleum, in nodular masses of needles, m. p. 115·5—117° after softening at 108°; when slowly heated above the m. p., the ester resolidifies, and then has m. p. 121°. It has b. p. 200°/12 mm. The 1 : 4- and the 2 : 4-dimethyl esters are both syrups, and the solution of the ammonium salt of the former gives a precipitate with concentrated solutions of copper sulphate, whilst that of the latter is precipitated even in dilute solution. The trimethyl ester has b. p. 194°/12 mm. (corr.), and solidifies in a freezing mixture at −13° to a vitreous mass.

The 1-*amide*, $NH_2{\cdot}CO{\cdot}C_6H_3(CO_2H)_2$, is obtained by heating the corresponding ester with a concentrated solution of ammonia in methyl alcohol at 100° for one and a-half hours, then acidifying, removing trimellic acid by extracting with ether, and extracting several times with amyl alcohol. After removal of the amyl alcohol and recrystallising the residue from a mixture of methyl alcohol and benzene, the amide is obtained pure, and has m. p. 185—186°. The isomeric 2-*amide*, obtained by a similar method, has m. p. 199—200°. The 1-amide reacts with bromine and alkali, yielding 4-amino-*iso*phthalic acid, which was isolated in the form of its methyl ester (m. p. 130°). The 2-amide under similar conditions yields aminoterephthalic acid, which was isolated as its methyl ester, m. p. 123—126° (Cahn-Speyer, Abstr., 1907, i, 849, gives m. p. 133°). By the action of a methyl-alcoholic solution of ammonia on the anhydro-acid, a mixture of the 1- and 2-amides is obtained. J. J. S.

Ring Synthesis of Pyromellitic Acid. FRANZ FEIST (*Ber.*, 1911, 44, 135—138).—Small amounts of pyromellitic acid (14% yield) are formed according to the equation: $2CO_2Et\cdot CH_2\cdot CHBr\cdot CHBr\cdot CO_2Et + 8KOH = C_6H_2(CO_2K)_4 + 4KBr + 4EtOH + 4H_2O + H_2$ when ethyl $\alpha\beta$-dibromoglutarate is mixed with alcoholic potassium hydroxide solution. The acid is isolated by acidifying the potassium salt and extracting eighteen times with ether. It is accompanied by large quantities of oily impurities, which can be removed by stirring with a small amount of ether in which the impurities dissolve. The anhydrous acid has m. p. 275°, and the tetramethyl ester, m. p. 141·5°.

J. J. S.

Preparation of Diglycollyldisalicylic Acid. CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P. 227999).—*Diglycollyldisalicylic* [*o-diglycollyloxybenzoic*] *acid*, $O(CH_2\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H)_2$, glistening leaflets, m. p. 168—170°, is readily prepared by boiling salicylic acid (or a salicylate) in benzene solution with diglycollic anhydride in the presence of an indifferent base (such as pyridine); it is of therapeutic importance, and compares favourably with acetylsalicylic acid in this respect.

F. M. G. M.

An *o*-Hydroxyaldehyde of Triphenylcarbinol. AUGUST BISTRZYCKI and MARTIN FELLMANN (*Ber.*, 1910, 43, 3579—3586).—Salicylaldehyde can be condensed with benzylic acid, forming 4-hydroxy-3-aldehydotriphenylacetic acid (Abstr., 1910, i, 321), and this by the elimination of carbon dioxide is readily converted into 4-hydroxy-3-aldehydotriphenylcarbinol, which is the third aldehyde of the triphenylmethane series to be described.

4-Hydroxy-3-aldehydotriphenylacetic acid, prepared by the condensation of the components in benzene in presence of tin tetrachloride, crystallises, $+\frac{1}{2}C_7H_8$, in microscopic prisms or needles, m. p. 198—200° (from toluene), or in stellar aggregates of prisms, $+\frac{1}{2}C_6H_6$, m. p. 197—198° (from benzene).

The *azine*, $N_2[:CH\cdot C_6H_3(OH)\cdot CPh_2\cdot CO_2H]_2$, derived from the action of hydrazine sulphate and sodium carbonate, is a yellow powder (decomp., 270—280°); the *sodium* salt crystallises in slender, yellow needles. The *oxime* crystallises in microscopic, colourless needles, which turn yellow at 110°, m. p. 226° (decomp.). The *semicarbazone* forms bunches of microscopic, slender, prismatic needles, m. p. 198—199° (decomp.). The *aniline* derivative is a granular, yellow powder, m. p. 85—86° (decomp.).

Methyl 4-*methoxy*-3-*aldehydotriphenylacetate*, prepared by the action of methyl sulphate in cold sodium hydroxide solution, crystallises in bunches of faintly yellow-coloured, four-sided prisms, m. p. 148—149°.

4-*Benzoxy*-3-*aldehydotriphenylacetic acid* crystallises in concentrically-grouped, colourless needles, m. p. 195·5—196·5°.

4-Hydroxy-3-aldehydotriphenylcarbinol (*loc. cit.*), prepared by the action of concentrated sulphuric acid on the aldehydo-acid, crystallises in aggregates of light yellow, prismatic plates, m. p. 123—124°, decomp. at 170°. The solution in concentrated sulphuric acid is

orange-red; a second isomeric form could not be obtained. The *acetyl* derivative crystallises in reniform aggregates of colourless prisms, m. p. 131—132°, the fused mass being orange-yellow. The *phenylhydrazone* forms rounded aggregates of microscopic prisms, decomp. 177°. The *oxime* separates in bunches of colourless, flat prisms; on heating, it becomes yellow and softens at 95°, becomes colourless, and solid again at 102°, m. p. 151° (decomp. 175°). The *semicarbazone* crystallises in colourless, microscopic needles, which become yellow at 140° and decompose at 164°, with an intense red coloration.

On heating the hydroxyaldehydocarbinol in a stream of dry air in a sulphuric acid bath at 190—200°, the anhydride, 2-*aldehydodiphenylquinomethane*, $CPh_2{:}C_6H_3O{\cdot}CHO$, is obtained as a brown powder. This darkens in colour at 100°, and begins to melt indefinitely at a somewhat higher temperature. E. F. A.

Hexahydroacetophenone [*cyclo*Hexyl Methyl Ketone] and **Hexahydrobenzoylacetone.** Marcel Godchot (*Compt. rend.*, 1910, 151, 1131—1134).—Adipic acid is the sole product of the oxidation of *cyclo*hexyl methyl ketone by alkaline potassium permanganate. *cyclo*Hexyl methyl ketone (Bouveault, Abstr., 1904, i, 61) forms an *oxime*, b. p. 145—150°/20 mm., m. p. 60°; no isomeric form was detected. It undergoes the Beckmann change, forming *acetylaminocyclohexane* (*hexahydroacetanilide*), $C_6H_{11}{\cdot}NHAc$, crystallising in needles, m. p. 103°, identical with the product obtained by acetylating *cyclo*hexylamine.

Hexahydrobenzoylacetone, $C_6H_{11}{\cdot}CO{\cdot}CH_2{\cdot}COMe$, is obtained in the form of its *sodium* salt by the addition of sodium ethoxide to a mixture of *cyclo*hexyl methyl ketone and ethyl acetate. The diketone has b. p. 103—105°/25 mm., D^{15} 0·9933, and was prepared in the pure state from its *copper* derivative, which crystallises in pale green needles m. p. 210°; the phenylhydrazone and oxime appear to be oily. W. O. W.

Ketones Derived from *o*-, *m*-, and *p*-Toluic Acids. Jean B. Senderens (*Compt. rend.*, 1911, 152, 90—92. Compare Abstr., 1909, i, 286, 627; 1910, i, 11, 179, 489).—The under-mentioned ketones have been prepared by passing the vapour of an aromatic and an aliphatic acid over thorium oxide at 460—470°. A single distillation of the product usually suffices to yield the aromatic ketone in a state of purity. The new ketones are liquids; their odour resembles that of citrons in the case of the ortho-compounds, and of fennel in the case of the para-derivatives; the odour of the meta-compounds is not characteristic. The b. p.'s given are corrected.

o-Tolyl methyl ketone, b. p. 211°/745 mm., D_4^0 1·0262; *semicarbazone*, m. p. 192°. *m*-Tolyl methyl ketone, b. p. 221°/745 mm., D_4^0 1·0165; *semicarbazone*, m. p. 188° (decomp.). *p*-Tolyl methyl ketone, b. p. 224·5°/745 mm., D_4^0 1·0150; *semicarbazone*, m. p. 200°. *o*-Tolyl ethyl ketone, b. p. 224°/745 mm., D_4^0 1·0119; *semicarbazone*, m. p. 169°. *m*-Tolyl ethyl ketone, b. p. 234°/745 mm., D_4^0 1·0059; *semicarbazone*, m. p. 166°. *p*-Tolyl ethyl ketone, b. p. 238°/745 mm., D_4^0 1·0053; *semicarbazone*, m. p. 180°. *o-Tolyl propyl ketone*, b. p. 238·5°/758 mm.,

D_4^0 0·9936; *semicarbazone*, m. p. 176°. m-*Tolyl propyl ketone*, b. p. 247°/758 mm., D_4^0 0·9882; *semicarbazone*, m. p. 152°. p-*Tolyl propyl ketone*, b. p. 251·5°/758 mm., D_4^0 0·9774; *semicarbazone*, m. p. 190°. o-*Tolyl* iso*propyl ketone*, b. p. 230°/758 mm., D_4^0 0·9858; the *semicarbazone* is an oil. m-*Tolyl* iso*propyl ketone*, b. p. 238°/758 mm., D_4^0 0·9841; *semicarbazone*, m. p. 120°. p-Tolyl *iso*propyl ketone, b. p. 243°/758 mm., D_4^0 0·9778; *semicarbazone*, m. p. 101°. o-*Tolyl* iso*butyl ketone*, b. p. 247·5°/758 mm., D_4^0 0·9744; *semicarbazone*, m. p. 166°. m-*Tolyl* iso*butyl ketone*, b. p. 254°/758 mm., D_4^0 0·9712; *semicarbazone*, m. p. 172°. p-*Tolyl* iso*butyl ketone*, b. p. 259°/758 mm., D_4^0 0·9707; *semicarbazone*, m. p. 212°. W. O. W.

Quinones. Hermann Haakh (*J. pr. Chem.*, 1910, [ii], **82**, 546—551).—A theoretical paper in which an attempt is made to account for the recent numerous examples of the formation of highly-coloured additive compounds of *p*-benzoquinone with inorganic acids and salts, aromatic hydrocarbons, and other substances. The author assumes that the comparatively feebly-coloured *p*-benzoquinone itself has Graebe's peroxide constitution, in which the oxygen atoms have no residual affinity; when it forms highly-coloured additive compounds, the quinone acquires the Fittig constitution, addition occurring by means of the residual affinity of the oxygen atoms. C. S.

Oxonium Hydrosulphides of *p*-Benzoquinone. M. M. Richter (*Ber.*, 1910, **43**, 3599—3603).—On mixing hydropersulphide and *p*-benzoquinone in anhydrous solvents at the ordinary temperature, a voluminous, brilliantly blue compound is obtained, which is labile in character and under certain conditions changes to a faintly yellow substance. The blue compound is obtained in presence of an excess of benzoquinone, the yellow with an excess of hydropersulphide.

The amorphous indigo-blue substance, *bis*-p-*benzoquinoneoxonium hydrotrisulphide*, $O{:}C_6H_4{:}O{<}^{H\ \ H}_{S{\cdot}S{\cdot}S}{>}O{:}C_6H_4{:}O$, decomposes at 115°, or when exposed to moisture. It dissolves in anhydrous solvents with an orange coloration, but is more or less decomposed.

By the action of *p*-benzoquinone dissolved in carbon disulphide and potassium hydrosulphide in absolute alcohol in a stream of hydrogen, *p-benzoquinoneoxonium hydrosulphide*, $O{:}C_6H_4{:}O{<}^{H}_{SK}$, is obtained as a dark greenish-black powder, extremely sensitive to traces of moisture.

Trisquinhydroneoxonium hydrosulphide, $C_{36}H_{32}O_{12}S$, is obtained by passing dry hydrogen sulphide through a solution of quinone in formic acid. It is a microcrystalline, almost black powder, decomp. 140°. The same compound is obtained on passing dry hydrogen sulphide over fused *p*-benzoquinone.

Hydropersulphide does not combine with substituted quinones; the entry of substituents, particularly of strongly negative groups, into the quinone molecule weakens the basic properties of oxygen and prevents salt formation. E. F. A.

Constitution of Quinhydrone-like Substances. M. M RICHTER (*Ber.*, 1910, **43**, 3603—3611).—The characteristics of oxonium salts, namely, simple addition of the components in their formation, ready decomposition in solution or when sublimed, and marked increase in the intensity of the colour, are also those of the quinhydrones. It is suggested that quinhydrones, phenoquinones, alloxantin, etc., are all to be regarded as oxonium compounds, and their dissociative and colour properties are due to quadrivalent oxygen and quinquevalent nitrogen. *p*-Benzoquinone has been shown (compare Siegmund, Abstr., 1909, i, 109; Meyer, *ibid.*, i, 395) to combine both with one and with two molecules of mono- and di-hydroxyphenols.

The evidence in favour of the formula $O{:}C_6H_4{:}O{<}^{H}_{O\cdot C_6H_4\cdot OH}$ for quinhydrone is discussed.

Two more must be added to the characteristics of the quinhydrones already enumerated, namely, they are composed of quinonoid and benzenoid sections, and they have the power of forming salts. The entry of substituting groups, particularly those of a strongly negative nature, into the quinone molecule materially lessens the basic properties of the oxygen atom, and in consequence prevents salt and quinhydrone formation.

Thirteen compounds are enumerated of six main types which are quinhydrone compounds of *p*-phenylenediamine, benzidine, and *p*-benzoquinonedichlorodi-imine.

It is considered that the simple oxygen atom generally behaves as a quadrivalent atom. E. F. A.

Preparation of *N*-Alkyl- and *N*-Arylaryl-sulphaminoanthraquinones. FRITZ ULLMANN (D.R.-P. 227324).—By the action of alkylsulphonamides of the general formula $R{\cdot}NH{\cdot}SO_2{\cdot}R_1$ (R = alkyl or aryl; R_1 = aryl) on halogenated anthraquinones, condensation products are obtained.

1-p*Toluenesulphonylphenylaminoanthraquinone*,

$$C_6H_4{<}^{CO}_{CO}{>}C_6H_3{\cdot}NPh{\cdot}SO_2{\cdot}C_7H_7,$$

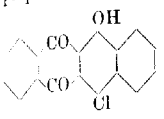
is prepared by heating together *p*-toluenesulphonylanilide and α-chloroanthraquinone in nitrobenzene solution in the presence of copper acetate and sodium carbonate; it crystallises from acetic acid in glistening, yellow crystals, m. p. 193°.

1-p-*Toluenesulphonylmethylaminoanthraquinone*, yellow needles, m. p. 192°, is prepared in a similar manner from *p*-toluenesulphonylmethylamide and α-chloroanthraquinone. By treatment with concentrated sulphuric acid, it yields α-methylaminoanthraquinone. F. M. G. M.

Preparation of 6-Chloro-1-hydroxynaphthacenequinone, and of 6-Chloro-1-hydroxynaphthacenequinone-4-sulphonic Acid. ANILINFARBEN and EXTRACT-FABRIKEN VORM. J. R. GEIGY (D.R.-P. 226230).—The work of Weizmann and others has shown that *o*-1-hydroxy-β-naphthoylbenzoic acid when heated with concentrated sulphuric acid and boric acid is converted quantitatively into 1-hydroxynaphthacenequinone (Trans., 1906, **90**, 116; 1907, **91**, 411;

1909, 93, 279); this reaction has now been extended to 4'-chloro-1'-hydroxy-β-naphthoyl-*o*-benzoic acid (Abstr., 1910, i, 746) and its sulphonic acids.

6-Chloro-1-hydroxynaphthacenequinone (annexed formula) was prepared by dissolving crystallised boric acid (6 parts) in 80 parts of concentrated sulphuric acid (25% SO_3), slowly adding the 4'-chloro-1'-hydroxy-β-naphthoylbenzoic acid (20 parts), and heating at 70° until sodium hydroxide ceased to produce a yellow coloration. The product after crystallisation from benzene formed long, reddish-yellow needles, m. p. 307°, and seems not to be identical with the 6-chloro-1-hydroxynaphthacenequinone, m. p. 290—293° (Trans., 1907, 91, 418). The *sodium* salt is insoluble in water.



6-Chloro-1-hydroxynaphthacenequinone-4-sulphonic acid was isolated in the form of its *monosodium* salt, a brick-red powder, by boiling with a saturated solution of sodium chloride; it is soluble in water with a yellow coloration; the *disodium* salt was obtained as a dark red gelatinous precipitate soluble in water with a blue coloration.

F. M. G. M.

Preparation of Alkyloxyacetyl Derivatives of Menthols. ALFRED EINHORN (D.R.-P. 225821).—The interaction of ethoxyacetic acid and mentholcarboxyl chloride in a cooled ethereal solution yields *menthol ethoxyacetate*, a colourless oil, b. p. 144°/14 mm. The reaction is a general one for the alkyloxyacetic acids and mentholcarboxyl halides. F. M. G. M.

Preparation of Santalyl Alkylaminoacetates. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 226229).—It is found that santalyl alkylaminoacetates of therapeutic importance can be prepared by treating chloroacetylsantalol with a secondary amine. *Chloroacetylsantalol*, a viscous, yellow oil, was prepared by treating santalol with chloroacetyl chloride in the presence of pyridine, or with chloroacetic acid, pyridine, and carbonyl chloride. This product was isolated, mixed with a solution of dimethylamine in benzene, and left during twenty-four hours; the *santalyl dimethylaminoacetate* was extracted with hydrochloric acid, and, on rendering the solution alkaline with sodium carbonate, separated as a yellow, odourless oil, which hydrolyses readily with alkalis into its components. It forms well characterised salts; the *hydrochloride* crystallises from acetone in odourless, colourless needles, m. p. 154°. Analogous compounds can be prepared with diethylamine or piperidine. F. M. G. M.

Catalytic Reactions at High Temperatures and Pressures. XXII. Reduction of Terpenes. WLADIMIR IPATIEFF (*Ber.*, 1910, 43, 3546—3553. Compare Sabatier and Senderens, Abstr., 1901, i, 459; Vavon, Abstr., 1910, i, 52, 400).—By reducing *l*-limonene with hydrogen at 280—300° under 110—120 atmospheres' pressure, using cupric oxide as the catalyst, an unsaturated hydrocarbon, $C_{10}H_{18}$, b. p. varying from 172° to 176°, is obtained. The same hydrocarbon is also

produced when copper is used, but a higher temperature is necessary. Further reduction of this hydrocarbon leads to the formation of *p*-menthane.

[With DRACHUSSOFF.]—French *l*-pinene in the presence of iron is not reduced, but undergoes isomerisation to dipentene. At 265° with cupric oxide as catalyst, it is reduced to a hydrocarbon, $C_{10}H_{18}$, whilst repeated reduction at 280—290° yields a hydrocarbon, $C_{10}H_{20}$, b. p. 163—170°, D^{20} 0·7949. Similar results were also obtained with metallic copper. With nickel oxide, the reduction takes place with great rapidity and at a lower temperature than with cupric oxide, $C_{10}H_{20}$ being formed.

It is considered probable that the hydrocarbon, $C_{10}H_{20}$, obtained from *l*-pinene consists of a mixture of *o*- and *p*-menthanes.

For the purpose of comparison, menthane was prepared from cymene by reducing with hydrogen, nickel oxide being used as a catalyst; it had b. p. 167—170°, D^{20} 0·8038. F. B.

Peppermint Oil Prepared from Dry Leaves of Mentha piperita. J. MURAOUR (*Bull. Soc. chim.*, 1911, [iv], **9**, 66—67).—Dry leaves, which had fallen naturally from mint plants during cultivation, gave a yield of from 400 to 500 grams of oil per 100 kilos. of leaves. This oil was yellow, and had an odour recalling that of Japanese peppermint oil. Two samples gave the following constants: D^{15} 0·911 to 0·913, $\alpha_D = -38°18'$ to $-40°4'$, solubility 1 in 1·5 to 2·5 vols. of alcohol at 80°, and contained 33·16 to 40·31% of esters and 43·99 to 45·67% of total menthol. The results of examination of commercial peppermint oils indicated that some of these products consisted of true peppermint oil of French origin mixed with oil from the fallen leaves. T. A. H.

Essential Oils. I. Orange Flower Oil. II. Schinus molle Oil. G. LALOUE (*Bull. Soc. chim.*, 1910, [iv], **7**, 1101—1107, 1107—1109).—A more detailed account of work already published (Abstr., 1910, i, 755; 1909, i, 817). Gildemeister and Stephan's observation (Abstr., 1897, i, 81) that *Schinus molle* oil contains pinene and phellandrene is confirmed, and there is probably also about 20% of sesquiterpenes present. Oil distilled from branches and leaves, obtained at Grasse, was richer in pinene than oil from leaves and branches obtained in Algeria. T. A. H.

Milk Sap of Antiaris toxicaria. HEINRICH KILIANI (*Ber.*, 1910, **43**, 3574—3579. Compare Abstr., 1897, i, 91).—Seligmann (Abstr., 1903, ii, 314) obtained from the juice of *A. toxicaria* procured from Sarawak an antiarin differing from that previously described. It is now found with juice obtained from Java that two antiarins exist, the new *β*-form being present in the larger proportion. They differ in crystalline form, melting point, water of hydration, and composition, although there is no difference in their toxic character.

α-Antiarin, $C_{27}H_{42}O_{10}.4H_2O$, crystallises in glistening plates or leaflets, m. p. 220—225°.

β-Antiarin, $C_{27}H_{38}O_{10}.3H_2O$ or $C_{28}H_{38}O_{10}.3H_2O$, crystallises in slender needles or bunches of columnar needles, m. p. 206—207°.

Emulsin is without action on either glucoside; the products of hydrolysis of β-antiarin have not been characterised. E. F. A.

Digitonin, Digitogenic Acid and their Oxidation Products. Heinrich Kiliani (*Ber.*, 1910 **43**, 3562—3574. Compare Abstr., 1904, i, 505).—A further study of the oxidation products of digitogenin shows that digitic acid has the composition $C_{28}H_{42}O_{11}$. Molecular weight determinations are particularly difficult to carry out in the case of oxidation products of digitogenic acid. It has not been found possible so to conduct oxidation as to obtain simple products of known constitution; even with ozone, the chief product is an acid, $C_{26}H_{40}O_7$.

To prepare digitonin, German digitalis is extracted with alcohol ether, the insoluble residue is dissolved in water, the vessel placed in a bath of water at 70°, a small quantity of amyl alcohol added, and, after inoculation, the whole is allowed to cool slowly until crystallisation is complete.

Digitic acid is tribasic, the barium salt being $(C_{28}H_{41}O_{12})_2Ba_3,18H_2O$. The normal potassium salt is hygroscopic, and the acid salt admixed with free acid; the calcium salt is amorphous, so that neither is suitable for analysis. The by-products of the oxidation consisted of acids miscible with sodium chloride solution, from which no chemical individual could be isolated, and of acids insoluble in salt solution. When further oxidised with permanganate in strongly alkaline solution, a definitely crystalline calcium salt, $C_{19}H_{26}O_7Ca,8H_2O$, was obtained (compare Kiliani and Baylen, Abstr., 1895, i, 65). The acid is indefinitely crystalline, m. p. 170° (decomp.).

Anhydrodigitic acid, when oxidised with potassium permanganate in neutral solution, forms an acid, $C_{26}H_{38}O_7$, crystallising in crusts of small pyramids, m. p. 196—200°; the magnesium salt crystallises in needles and small pyramids.

From the products of oxidation of digitogenic acid by hot permanganate in neutral solution, a new tribasic *acid*, $C_{28}H_{42}O_{11}$, has been isolated; it crystallises in leaflets, m. p. 155° (decomp.). The *barium* salt, $C_{28}H_{40}O_{11}Ba,10H_2O$, crystallises in aggregates of closely-packed needles and is strongly acid. The acid is isomeric with digitic acid.

On oxidation of digitogenic acid with ozone, more than 60% of an *acid*, $C_{26}H_{40}O_7$, is obtained; this crystallises in clusters of pyramids, m. p. 222°. A *magnesium* salt, $C_{26}H_{38}O_7Mg,11H_2O$, crystallises also in tiny pyramids. It has not been established in what form the two atoms of carbon are eliminated during the oxidation. E. F. A.

Saponification of Sinigrin. Max Gonnermann (*Pflüger's Archiv*, 1911, **137**, 453—469).—Sinigrin is not acted on by any enzyme with the exception of myrosin. The enzymes investigated under varying conditions of solvent, etc., were of both animal and vegetable origin; bacteria, including those in the intestine, have no effect in liberating allylthiocarbimide. This confirms Kobert's statement. Various details regarding the mode of preparation of this glucoside are given. W. D. H.

A Saponin-Cholesterol Compound. S. YAGI (*Arch. exp. Path. Pharm.*, 1910, **64**, 141—146).—Ransom having shown that cholesterol inhibits the hæmolytic power of saponin, Windaus found that certain saponins form additive products with cholesterol; the digitonin-cholesterol compound, for instance, is crystallisable, and has the formula $C_{82}H_{140}O_{29}$, that is, a combination of one molecule of each substance ($C_{55}H_{94}O_{28} + C_{27}H_{46}O$). Other cholesterides have been separated by the same author. The present paper gives details of the preparation and properties of another crystallisable cholesteride, namely, that of dioscine, in which three molecules unite with two of cholesterol, $3C_{24}H_{38}O_6.2C_{27}H_{46}O,1$ or $2H_2O$, a microcrystalline powder, m. p. 223°; this is inactive on blood corpuscles. The feeble hæmolytics, such as Merck's saponin, sapotoxin, and dioscorea-sapotoxin, need about an equimolecular amount of cholesterol to render them inactive; half the amount leaves them still partly active; the feeble members of the group therefore do not contain active mixed with inactive molecules.

W. D. H.

Action of Nitric Acid on Aloins; Production of Tetranitroaloe-emodin and of 2 : 4 : 6-Trinitro-3-hydroxybenzoic Acid. EUGÈNE LÉGER (*Compt. rend.*, 1910, **151**, 1128—1131; *Bull. Soc. chim.*, 1911, **9**, 88—97).—It has long been known that chrysammic acid and picric acid are amongst the products of the action of nitric acid on the aloins. It is now shown that the production of these compounds is preceded by the formation of two other substances, which are then converted into these acids by the further action of nitric acid.

Tetranitroaloe-emodin, $C_{15}H_6O_5(NO_2)_4$, arises from the action of nitric acid (D 1·2) on barbaloin or *iso*barbaloin at the temperature of the water-bath. It occurs in slender, golden needles, m. p. about 285° with deflagration. On long boiling with nitric acid (D 1·32), it is converted into chrysammic acid.

The mother liquor from the tetranitroaloe-emodin contains 2 : 4 : 6-trinitro-3-hydroxybenzoic acid (Griess, *Annalen*, 1861, **117**, 28); this crystallises from ether in almost colourless, efflorescent, rhombic lamellæ, m. p. 185·5—186·5° (corr.). It loses carbon dioxide when heated with nitric acid, and forms picric acid.

Tetranitrorhein, $C_{14}HO_3(NO_2)_4(OH)_2{\cdot}CO_2H$, is probably an intermediate product in the conversion of tetranitroaloe-emodin into chrysammic acid. It has been isolated as short, efflorescent prisms.

W. O. W.

Chlorophyll. X. Comparative Investigation of Chlorophyll from Different Plants. II. RICHARD WILLSTÄTTER and ALFRED OPPÉ (*Annalen*, 1910, **378**, 1—18. Compare Willstätter, Hocheder, and Hug, Abstr., 1910, ii, 150).—An examination of the leaves of 200 species of plants has shown that the chlorophyll present is the so-called amorphous or wax-like form which yields phytol. The phæophytin obtained from the dried leaves gives a 33% yield of phytol, provided the extraction is carried out rapidly. In

many cases, for example, grass and plantains, good yields of phytol are also obtained when a slow method of extraction is used, but in others the amount of phytol isolated diminishes as length of time taken for the extraction is increased. Thus the yields of phytol from *Heracleum spondylium* are 6·0 when the extraction takes twenty-four hours, 20·2 for one hour, and 31·5% for three-quarters of an hour.

It is evident that the chlorophyll loses its phytol when its alcoholic solution is left in contact with the plant tissues, and this loss is due to enzyme action (Willstätter and Stoll, next abstract). The results account for the low percentages of phytol obtained in previous experiments (*loc. cit.*), as the slow method of extraction was used. The increase observed in the amount of phytol when the dried material is kept can be accounted for by the enzyme losing its activity with age.

Two quick methods of extraction are described. The one consists in rubbing the leaf powder with chalk and sufficient alcohol to form a thick paste (about 1 litre per kilo. of leaf powder), leaving for five minutes, filtering under pressure, and washing with small amounts of alcohol. The second method consists in making a much stiffer paste, 300 c.c. of alcohol for 1 kilo. of powder, and placing on a percolator and using low pressures. This second method is the better when comparatively concentrated solutions of chlorophyll are required.

The phæophytin was obtained by the addition of oxalic acid to the extract. When chlorophyll had not undergone decomposition, a fine compact precipitate of phæophytin mixed with oxalates was obtained, but if much phytol has been formed, the precipitate had a voluminous, coagulated appearance.

Phytochlorin-*e* and phytorhodin-*g* have been isolated from the phæophytin from 125 different plant species. The amount of phytorhodin-*g* diminishes as the boiling with the alcoholic potassium hydroxide is increased, or as the concentration of the alkali is increased. In many cases a phytochlorin somewhat more feebly-basic than phytochlorin-*e* was isolated. The usual method of hydrolysis was boiling for two to three hours with 24% methyl-alcoholic potassium hydroxide, using 5 c.c. of solution for 1 gram of phæophytin. J. J. S.

Chlorophyll. XI. Chlorophyllase. Richard Willstätter and Arthur Stoll (*Annalen*, 1910, 378, 18—72).—Willstätter and Oppé (preceding abstract) have shown that the conversion of amorphous chlorophyll into crystallised chlorophyll is accompanied by the elimination of a phytol group, and that the change occurs when the process of extraction is slow, but can be avoided by using a rapid method of extraction. It is now shown that crystallised chlorophyll contains one methoxy- and one ethoxy-group and not two methoxy-groups (Willstätter, Hocheder, and Hug, Abstr., 1910, ii, 150), and that the amorphous chlorophyll contains one methoxy- and one phytyl group; it is proved that the change of the amorphous into the crystallised chlorophyll is a process of alcoholysis, and in each stage of the change the phytol eliminated is equivalent to the ethyl alcohol

entering the molecule. The reaction, which is represented by the equation:

$$CO_2H\cdot C_{31}H_{29}N_4Mg(CO_2Me)\cdot CO_2\cdot C_{20}H_{39} + EtOH = C_{20}H_{39}\cdot OH + CO_2H\cdot C_{31}H_{29}N_4Mg(CO_2Me)\cdot CO_2Et,$$

takes place in the presence of a specific enzyme, *chlorophyllase*, which belongs to the group of esterases. Other substances of the same group, for example, lipase from linseed or pancreas lipase, cannot bring about the same change. The enzyme reacts slowly with phæophytin, and does not react at all with waxes of an ester nature. It is highly probable that the enzyme brings about the formation of phytyl esters in the plant. Working with methyl alcohol, it has been found possible to replace the phytoxyl groups by methoxyl (methanolysis) and in the presence of moist ether to replace the phytoxyl group by hydroxyl (hydrolysis). Lipases, on the other hand, produce hydrolysis, but do not appear able to induce alcoholysis.

The following system of nomenclature is suggested for chlorophyll derivatives: the tricarboxylic acid, $C_{31}H_{29}N_4Mg(CO_2H)_3$, from which chlorophyll is derived is called *chlorophyllin*; the monomethyl ester obtained by the hydrolysis of chlorophyll is termed *chlorophyllide*; amorphous chlorophyll is *phytylchlorophyllide*; Borodin's crystallised chlorophyll is *ethylchlorophyllide*; the magnesium-free compound,

$$C_{31}H_{31}N_4(CO_2H)_3,$$

is termed *phaeophorbide*; phæophytin is thus *phytylphaeophorbide*, and the compound hitherto called phæophorbin is *ethylphaeophorbide*.

A rapid method for the extraction of chlorophyll is described which differs somewhat from those recommended by Willstätter and Oppé (preceding abstract). It consists in moistening 1 kilo. of the leaf meal for five minutes with 0·5 litre of alcohol (96%), then spreading on a thimble, and applying suction for a short time. The addition of alcohol, and suction, are used alternately until a further litre of alcohol has been added; in the course of twenty minutes, 1 litre of solution is obtained; by washing with alcohol, a further 0·9 litre of extract is obtained in thirty-five minutes more. The amount of chlorophyll in the two extracts is 80% of the total present. The solutions, although dilute, are purer than those obtained by the methods already described, and therefore yield more phæophytin.

For the estimations of phytol the method already described (Abstr., 1910, ii, 150) has been used. The amount of chlorophyll transformed into ethylchlorophyllide by means of chlorophyllase has been determined both by the estimation of the phytol liberated and by determining the amount of silver iodide obtained from the product by Zeisel's method. Details for the calculations are given. The results obtained by the two methods agree, indicating that the ethyl groups entering the molecule are equivalent to phytyl groups removed. It is highly probable that the reaction is a direct exchange of alkyl for phytyl groups, and that it does not consist in the hydrolysis of the phytyl ester to the acid and the subsequent conversion of this into the ethyl ester. The enzyme was in the form of leaf meal from which the chlorophyll had been extracted, and was used whilst moist with alcohol. The reaction was most rapid when the mixture was kept well shaken, and in each experiment the flasks were well corked in order to prevent

the admission of moisture. Although the reaction mixture is non-homogeneous, it is probable that the diffusion phenomena are such that the mixture behaves as if it were a homogeneous one. The values of K, however, when calculated by means of the equation for a unimolecular reaction, are not constant, but diminish as t increases. This is shown to be due partly to the fact that the enzyme tends to become less active when kept for some time. With varying amounts of enzyme, Schütz's rule, $\mu = K\sqrt{E.t}$, holds good approximately. With chlorophyll solutions of different concentrations, the amount transformed in a given time is roughly proportional to the concentration. The addition of water to the alcoholic solutions accelerates the activity of the chlorophyllase; thus the value of $K \times 10^3$ after ten hours varies from 28 to 37 using 92% alcohol, but with 80% alcohol $K \times 10^{13}$ has the values 175, 166, and 80. Even in 80% alcohol the reaction is a true alcoholysis and not hydrolysis. The activity of the enzyme is less at 35° than at 25°; when boiled with alcohol the enzyme is gradually destroyed, and in drying leaves for the preparation of the enzyme it is necessary to avoid high temperatures. Calcium carbonate has no effect on the alcoholysis, whereas magnesium hydroxide has an appreciable retarding effect. Young leaves appear to contain a smaller amount of enzyme than older ones, and the amount tends to increase as the chlorophyll increases.

The methylchlorophyllide, obtained by using methyl in place of ethyl alcohol, is formed much less readily, and its isolation is rendered difficult by the readiness with which it is transformed into readily soluble derivatives. The reaction proceeds more readily in the presence of a small amount of water, for example, in 92% methyl alcohol, but the best results are obtained by treating fresh leaves with 50—60% methyl alcohol. The product varies with the species of plant used; that obtained from *Heracleum*, $C_{73}H_{70}O_{11}N_8Mg_2$, crystallises from ether, in which it is sparingly soluble, in steel-blue, glistening prisms. The corresponding *methylphaeophorbide*, $C_{72}H_{74}O_{11}N_8$, forms glistening, spindle-shaped crystals with a metallic lustre. The methylchlorophyllide from stinging nettles is somewhat more readily soluble in ether, and crystallises in triangular and hexagonal plates.

Chlorophyllide, $CO_2Me{\cdot}C_{31}H_{29}N_4Mg(CO_2H)_2$, may be obtained by the action of the enzyme on a moist ethereal solution of chlorophyll in the absence of alcohol. It forms green plates and is extremely unstable, and is transformed readily into the isomeric *magnesium phaeophorbide*, $CO_2Me{\cdot}C_{31}H_{31}(CO_2)_2Mg$, which forms black crystals readily decomposed by acid.

The synthesis of chlorophyll from chlorophyllide and phytol can be accomplished by means of chlorophyllase, but the yields are small. Chlorophyll always appears to be accompanied by chlorophyllase; in *Sorbus aucuparia*, *Mellitis melissoph.*, *Stachys silvitica*, *Lamium maculatum*, and *Heracleum* the amount of enzyme is comparatively large. The presence of the enzyme in stinging nettles, grass, *Sambucus*, *Aspidium*, *Equisetum*, *Taxus*, *Avena*, and *Platanus* can be demonstrated by the prolonged action of the tissue on the chlorophyll extract, when products are obtained which contain but little combined phytol.

Extracts of stinging nettles and of *Platanus* react with the enzyme

from *Galeopsis* or *Heracleum* more readily than with their own enzymes, but the alcoholysis does not proceed to completion. Under conditions which result in the complete alcoholysis of the chlorophyll of *Galeopsis* or *Heracleum*, only 66% of the chlorophyll of stinging nettles is decomposed. The chlorophyll of *Heracleum* reacts only slowly with stinging-nettle meal, but the rate is greater than that between stinging-nettle meal and the chlorophyll from stinging-nettle extract. J. J. S.

Chlorophyll. XII. Phytol I. Richard Willstätter, Erwin W. Mayer, and Ernst Hüni (*Annalen*, 1910, **378**, 73—152. Compare Willstätter and Hocheder (Abstr., 1907, i, 784).—Crude phytol and the distilled product are not identical but isomeric, and the process of distillation appears to produce a shifting of a double linking. The two are termed respectfully α- and β-phytol. An examination of the products of oxidation shows that the α-compound has the olefine linking between carbons 5 and 6, as it yields a ketone, $C_{15}H_{30}O$, whereas β-phytol yields a ketone, $C_{13}H_{26}O$, and contains an olefine linking between carbons 7 and 8. The chief oxidation products isolated are the following ketones and acids. (1) Ketone, $C_{15}H_{30}O$, obtained from α-phytol by means of chromic anhydride, or from the α-ozonide. (2) Ketone, $C_{13}H_{26}O$, from β-phytol by means of chromic anhydride, from the β-ozonide, or from the acid $C_{14}H_{28}O_2$ by means of chromic acid. (3) Ketone, $C_{11}H_{22}O$, from trihydroxyphytan and chromic acid, or by the action of ozone on the ketones 1 and 2. (4) Ketone, $C_9H_{18}O$, by the action of ozone on any of the other ketones. (5) Acid, $C_{14}H_{28}O_3$, from α-phytol and ozone, from trihydroxyphytan and chromic acid, or from the ozonide of the olefine $C_{15}H_{30}$. (6) Acid, $C_{12}H_{24}O_2$, from the ketone, $C_{15}H_{30}O$ and ozone, from the ketone $C_{13}H_{26}O$ and chromic acid, or from the acid $C_{14}H_{28}O_2$ and chromic acid. (7) Acid, $C_{10}H_{20}O_2$, from the ketone $C_{15}H_{30}O$ and ozone, and from the ozonide of the olefine $C_{15}H_{30}$.

The first two ketones are easily obtained in a state of purity, but the two lower ones are more difficult to prepare. They are all methyl ketones, although they yield only traces of bromoform with hypobromite and only small amounts of methylamine by the Beckmann transformation. The presence of the acetyl group in the ketone $C_{15}H_{30}O$ can be demonstrated by the following series of reactions: $C_{13}H_{27}\cdot CO\cdot CH_3 \longrightarrow C_{13}H_{27}\cdot CH(OH)\cdot CH_3 \longrightarrow C_{13}H_{27}\cdot CHCl_2 \rightarrow C_{13}H_{27}\cdot CH(OH)\cdot CH_2\cdot OH \longrightarrow C_{13}H_{27}\cdot CO_2H$. The four ketones resemble one another in physical properties. They are pale yellowish-green oils with relatively high b. p.'s, and it is suggested that the compounds, especially the lower members, have the tautomeric enolic structure. The acids are saturated and do not decolorise bromine, but react readily with permanganate. They do not crystallise, and resemble phytol in physical properties.

The reduction products of phytol and also numerous esters have been prepared.

α-Phytol contains the double linking in the βδ-position with respect to the $CH_2\cdot OH$-group, as the phytenic acid obtained by oxidising with chromic acid is an αβ-unsaturated acid, and the following structural

formula is suggested: $CHMe_2\cdot[CHMe]_3\cdot CMe{:}CMe\cdot CHMe\cdot CH_2\cdot OH$. It is possible that *α*-phytol is a condensation product of isoprene,

$$4C_5H_8 + H_2O + 3H_2 = C_{20}H_{40}O.$$

The formula suggested for *β*-phytol is

$$CHMe_2\cdot[CHMe]_4\cdot CMe{:}CMe\cdot[CHMe]_2\cdot CH_2\cdot OH.$$

α-Phytol has D_4^{20} 0·856 and n_D^{20} 1·46364, and *β*-phytol, D_4^{20} 0·852 and n_D^{20} 1·46380. It can be distilled in portions of 10—30 grams from Claisen flasks, and has b. p. 203—204°/9—10 mm. Both compounds give the same iodine number. A good test for the presence of phytol, for example, in phæophytin preparations, is the formation of a stable, colourless oil by heating for a short time with concentrated nitric acid. When the boiling is prolonged, a nitrogenous acid is formed, the alkaline solutions of which have an intense yellow colour. Many phytol preparations, both crude and distilled, undergo autoxidation (Engler and Weissberg, Abstr., 1899, *i*, 189) when kept for several months in corked vessels. A sharp, penetrating odour with an acid reaction is noticeable, and the oil becomes limpid and, at the same time, distinctly acid. The formation of a peroxide can be detected by Engler's method. The rate of autoxidation varies considerably with different samples, and it is probable that small amounts of some impurity, present in both the crude and the distilled products, act as a catalyst. The acid formed is not homogeneous and is unsaturated; the analytical numbers indicate that it may be a mixture of equal amounts of phytenic acid and a saturated acid with 10 carbon atoms.

Phytyl hydrogen phthalates, $CO_2H\cdot C_6H_4\cdot CO_2\cdot C_{20}H_{39}$, are formed when the phytol and phthalic anhydride are boiled for five hours with benzene, and can be isolated by making use of the fact that their sodium salts are very sparingly soluble in water, but are soluble in ether. The *α*-phytyl ester is a syrup, readily soluble in most organic solvents; it yields an oily *dibromide*, which is unstable, and a *silver* salt, $C_{28}H_{43}O_4Ag$, in the form of minute, flat prisms, m. p. 119°; the isomeric *silver β-phytyl phthalate* crystallises in prisms, m. p. 116°.

Cetyl hydrogen phthalate, $CO_2H\cdot C_6H_4\cdot CO_2\cdot C_{16}H_{33}$, forms indefinite crystals of a waxy consistency, and has m. p. 61—62°. The *silver* salt, $C_{24}H_{37}O_4Ag$, crystallises from benzene.

Phytyl ether, $O(C_{20}H_{39})_2$, obtained by the action of concentrated sulphuric acid on a glacial acetic acid solution of the alcohol, is a viscid oil sparingly souluble in glacial acetic acid or in methyl alcohol, and forms a dibromide.

Phytol cannot be reduced by means of sodium and ethyl or amyl alcohol, but by electrolytic reduction in cold alcoholic sulphuric acid solution, using platinised platinum electrodes with a voltage of 6 and a current density of 3 ampere per sq. m. and an earthenware diaphragm, the saturated alcohol, *phytanol* (*dihydrophytol*), $C_{20}H_{42}O$, is obtained together with the hydrocarbon phytan. Phytanol is readily prepared by reducing phytol with hydrogen in ethereal solution, using platinum-black as catalyst; a slow stream of hydrogen is passed through for about three weeks when 40 grams of phytol are used. The reduction is much quicker when the hydrogen is used under slight pressure and the apparatus is shaken continuously. It is a colourless, odourless oil, has b. p. 201·5—202°/9·5 mm., is miscible with all organic

solvents, and is isomeric with arachyl alcohol (Haller, Abstr., 1907, i, 377). It forms a *sodium* derivative, $C_{20}H_{41}\cdot ONa$, in the form of a viscid oil, soluble in ether or light petroleum.

The *phenylurethane*, $NHPh\cdot CO\cdot O\cdot C_{20}H_{41}$, obtained by the combination of the alcohol with phenylcarbimide, is also a thick oil. *Phytanyl hydrogen phthalate*, $CO_2H\cdot C_6H_4\cdot CO_2\cdot C_{20}H_{41}$, is a syrup, and its *silver* salt, $C_{28}H_{45}O_4Ag$, has m. p. 106—106·5°. *Phytanyl pyruvate*,

$$CH_3\cdot CO\cdot CO_2\cdot C_{20}H_{41},$$

obtained by heating the components at 110—120°, or more readily by shaking the alcohol for a long time at the ordinary temperature with five times its weight of pyruvic acid and removing the excess of acid by means of water, has b. p. 219—220°/10 mm.; its *semicarbazone*, $C_{23}H_{47}O_3N_3$, crystallises from methyl alcohol in needles, m. p. 88—91°. *Cetyl pyruvate* has m. p. 26·5—27·5°, and its *semicarbazone*, $C_{19}H_{39}O_3N_3$, crystallises in flat prisms, m. p. 140—141°.

The esterification of β-phytol by means of glacial acetic acid at 155° has been studied; at the end of one hour, 34·5% of the acid is transformed into ester, but after one hundred and forty-four hours the yield has fallen to 6·9%, owing to decomposition of the ester into phytadiene. Geraniol and nerol react in much the same manner with glacial acetic acid at 155°. The initial rates of esterification with acetic acid at 155° of the following unsaturated alcohols have been determined: oleyl alcohol, erucyl alcohol, geraniol, nerol, cholesterol, and the values obtained are smaller than those for the corresponding saturated alcohols. *Erucyl alcohol*, $C_{22}H_{44}O$, prepared by reducing ethyl erucate with boiling amyl alcohol and sodium, has b. p. 240·5—241·5°/10 mm., and forms rhombohedral crystals, m. p. 34·5—35·5°. Its *dibromide*, $C_{22}H_{44}OBr_2$, forms glistening prisms, m. p. 45—45·5°. When reduced with hydrogen in the presence of finely-divided platinum, the unsaturated alcohol yields *docosyl alcohol*, $C_{22}H_{46}O$, which crystallises from chloroform in glistening prisms, m. p. 71—71·5°; the *phenylurethane*, $C_{29}H_{51}O_2N$, crystallises from ethyl acetate in glistening prisms, m. p. 86—86·5°. The percentages of acetic acid transformed into ester at 155° are the following: dihydrophytol, 73; arachyl alcohol, 76·2; tetrahydrogeraniol, 68·3. These values are lower than those given by normal alcohols.

Phytanic acid, $C_{20}H_{40}O_2$, is best prepared by oxidising dihydrophytol with an acetic acid solution of chromic acid in the presence of potassium hydrogen sulphate, and forms a viscid oil, b. p. 221°/7·5 mm. The *silver* salt, $C_{20}H_{39}O_2Ag$, darkens at 165° and has m. p. 177—177·5°. The *amide*, $C_{19}H_{39}\cdot CO\cdot NH_2$, crystallises when its solutions in methyl alcohol or light petroleum are well cooled, and has m. p. 53—53·5°. *Δ³-Phytenic acid*, $C_{20}H_{38}O_2$, is formed together with the ketone, $C_{15}H_{30}O$, when phytol is oxidised with an acetic acid solution of chromic anhydride (5 atoms of O) in the presence of potassium hydrogen sulphate. It forms a yellow oil, b. p. 210—220°/11·5 mm., and has D_4^{20} 0·917 and n_D^{20} 0·893. The position of the ethylene linking is established by the readiness with which it yields a γ-lactone (Abstr., 1907, i, 786) when heated with sulphuric acid and water. The saturated hydrocarbon, *phytane*, $C_{20}H_{42}$, is most readily obtained by reducing phytene with hydrogen and platinum; it is a colourless,

mobile oil, with b. p. 169·5°/9·5 mm. and D_4^{20} 0·803, is only sparingly soluble in cold methyl alcohol, and solidifies when cooled by liquid air. In the preparation of phytene (Abstr., 1907, i, 786) a *di-iodo*-derivative, $C_{20}H_{40}I_2$, is obtained in the form of a heavy oil, and when this is reduced with zinc dust and glacial acetic acid, or with zinc dust and hydriodic acid, it yields impure phytene, although the two iodine atoms are not attached to adjacent carbon atoms. *Phytadiene*, $C_{20}H_{38}$, is formed when β-phytol, phthalic anhydride, and benzene are heated for a day in a Babo funnel, owing to the readiness with which the phytyl hydrogen phthalate decomposes into phytadiene and phthalic acid; it has b. p. 186—187°/13 mm. and D_4^{20} 0·826, and its iodine number points to the presence of two olefine linkings.

α-Phytol ozonide, prepared by passing a current of 6% ozone into a dry chloroform solution of the alcohol and then removing the chloroform under reduced pressure at 20°, forms a pale green syrup with a pungent odour, and dissolves readily in most organic solvents. Methyl alcohol separates the crude ozonide into an insoluble "moloxide," $C_{20}H_{40}O_4O_2$, and a soluble oxozonide, $C_{20}H_{40}O_4O_4$. The yield of the "*moloxide*" is larger the shorter the time of ozonising, and it can be obtained crystalline by well cooling its methyl alcoholic solution. It is an oil at the ordinary temperature, and when boiled with water yields the same products and in the same amounts as the oxozonide. This latter, when kept for some months under reduced pressure over phosphoric anhydride, yields the normal *ozonide*, $C_{20}H_{40}O_4O_3$.

The best yields of the ketone, $C_{15}H_{30}O$, are obtained when α-phytol is oxidised with a glacial acetic acid solution of chromic anhydride in the presence of potassium hydrogen sulphate. With the theoretical amount of oxygen, only a small amount of the alcohol is oxidised; but with 4 to 5 atoms of oxygen to each molecule of alcohol, a 73—97% yield of ketone can be obtained. The same ketone is also formed when either of the ozonides of α-phytol is boiled with water for three hours in a reflux apparatus, using 25 grams at a time. The aqueous solution has a decided acid reaction, and gives the ordinary reactions for aldehydes. The oily product consists of the ketone together with the acid $C_{14}H_{28}O_2$ (3·5%), phytenic acid, the hydrocarbon $C_{15}H_{32}$, and a small amount of an ether. The acids can be removed by extraction with very dilute sodium hydroxide solution, and the ketone purified by distillation under reduced pressure. It forms a pale yellowish-green, limpid oil, which turns quite colourless in the course of two to three weeks. It has b. p. 173—174°/9 mm. and 291·8—292·4°/722 mm., and is optically inactive. The *oxime*, $C_{15}H_{31}ON$, is a viscid oil with b. p. 201—202°/10 mm. and D_4^0 0·885; the *semicarbazone*, $C_{16}H_{33}ON_3$, crystallises from alcohol in well-developed prisms, m. p. 64·5°, and the *p-nitrophenylhydrazone*, $C_{21}H_{35}O_2N_3$, forms a pale yellow oil. The ketone combines with bromine in chloroform solution, yielding an unstable dibromide, which is probably derived from the isomeric enolic compound. Many ketones, for example, cholestanone and methyl ethyl ketone, form colourless dibromides in solution (compare also Linnemann, *Annalen*, 1863, **125**, 307; Lippmann, *Zeitsch. Chem.*, 1869, **5**, 29). The ketone gives negative results with the following reagents for aldehydes: sodium amalgam and diazobenzenesulphonic acid, benzenesulpho-

hydroxamic acid, pyruvic acid, and β-naphthylamine. It yields a peroxide, from which the ketones $C_{13}H_{26}O$ and $C_{11}H_{22}O$ are formed by boiling with water.

The *alcohol*, $C_{15}H_{32}O$, obtained by reducing the ketone with sodium and alcohol, is a colourless, viscid liquid, with b. p. 178—180°/12 mm. or 173—174°/8 mm., D_4^0 0·848, D_4^{20} 0·838, and n_D^{20} 1·44912. The saturated *hydrocarbon*, $C_{15}H_{32}$, occurs in the first fraction obtained by distilling the crude ketone under diminished pressure, and is deprived of the last traces of ketone by repeatedly shaking with three times its volume of glacial acetic acid, in which the ketone is readily soluble. It has b. p. 260·5—263·5°/723 mm. (corr.) or 127—130°/9·5 mm., D_4^0 0·789, D_4^{20} 0·779, and n_D^{20} 1·43322, and is also formed in small quantities when the ketone is reduced with zinc dust and glacial acetic acid. The *olefine*, $CH_2{:}CH{\cdot}CHMe{\cdot}C_{11}H_{23}$, obtained by the action of phosphoric oxide on the alcohol, $C_{15}H_{32}O$, at 60—70°, has b. p. 150—152°/11 mm. or 290°(corr.)/724 mm., D_4^0 0·803 and D_4^{20} 0·790, and combines readily with bromine. Its *ozonide*, $C_{15}H_{30}O_3$, is a viscid oil, with a pale green colour. When the alcohol $C_{15}H_{32}O$ is heated at 150° for an hour with phosphoric oxide, or when the above olefine is heated for several hours at 130° with the anhydride, a product is formed which contains a small amount of a saturated (cyclic) hydrocarbon.

The *ketone*, $C_{13}H_{26}O$, resembles its higher homologue; it has b. p. 168—170°/10 mm. or 288—289°/722 mm., D_4^0 0·865, D_4^{20} 0·848, and is optically inactive. It is not oxidised so readily as its homologue, $C_{15}H_{30}O$. The *oxime*, $C_{13}H_{27}ON$, is a viscid oil, b. p. 196—198°/11 mm. and D_4^0 0·891, and the *semicarbazone*, $C_{14}H_{29}ON_3$, forms slender needles, m. p. 62°. A 94% yield of the ketone is formed by oxidising β-phytol with a glacial acetic acid solution of chromium trioxide in the presence of potassium hydrogen sulphate, and an 82% yield by boiling β-phytol-ozonide with water. It is formed together with the acid $C_{16}H_{32}O_2$ (26—33%) by oxidising the ketone $C_{15}H_{30}O$ with a glacial acetic acid solution of chromium trioxide in the presence of concentrated sulphuric acid. A by-product formed at the same time is the *ether*, $O(C_{19}H_{21})_2$, which has b. p. 228—233°/722 mm. and D_4^0 0·836.

Trihydrocyphytane, $C_{20}H_{39}(OH)_3$, obtained by converting α-phytol dibromide into the acetate and subsequent hydrolysis, is a viscid oil, sparingly soluble in cold methyl alcohol, and when oxidised with chromium trioxide in the presence of glacial acetic and concentrated sulphuric acids yields the *ketone*, $C_{11}H_{22}O$, as a colourless, mobile oil, b. p. 168—170°/8 mm., together with the acid, $C_{14}H_{28}O_2$; its *semicarbazone*, $C_{12}H_{25}ON_3$, crystallises from alcohol in needles, m. p. 68—72°. The same ketone is formed when the product, obtained by the prolonged action of ozone on the ketone $C_{15}H_{30}O$, is boiled with water. The *ketone*, $C_9H_{18}O$, is a limpid oil, with b. p. 168°/10 mm. or 282°/720 mm., and has D_4^0 0·836. Its *semicarbazone* has m. p. 75°.

The olefine *dibromide*, $C_{15}H_{30}Br_2$, is a yellow oil, and, when shaken with silver acetate and glacial acetic acid at the ordinary temperature, yields the *bromoacetyl* derivative, $C_{15}H_{30}BrAc$, as a viscid oil, which reacts with silver acetate at 100°, yielding the *diacetate*, and this on hydrolysis with cold methyl-alcoholic potassium hydroxide yields an

ether of the glycol, $(C_{15}H_{30}\cdot OH)O$, as a brown, viscid oil. The ether, when oxidised with chromium trioxide, glacial acetic and sulphuric acids, yields as intermediate product a carbonyl *compound*, $C_{15}H_{30}O_2$, and ultimately the acid $C_{14}H_{28}O_2$. The same acid is also formed when the olefine ozonide is boiled for five hours with water, but appreciable amounts of the ester, $C_9H_{17}\cdot CO_2\cdot C_{10}H_{21}$, are also formed. The *acid*, $C_{14}H_{28}O_2$, is a colourless, comparatively viscid oil, with b. p. 186—188°/8—9 mm., D_4^0 0·887 and D_4^{20} 0·870. The *silver* salt, $C_{14}H_{27}O_2Ag$, is obtained crystalline by using alcoholic solutions, and has m. p. 186—188°.

The *acid*, $C_{10}H_{20}O_2$, is a colourless, odourless, viscid oil, b. p. 155—158°/11 mm. and 261°/722 mm., D_4^0 0·956, D_4^{20} 0·936, and n_D^{20} 1·45205; it decolorises permanganate in glacial acetic acid solution after a short time. The *silver* salt, $C_{10}H_{19}O_2Ag$, forms a crystalline precipitate, and with benzene forms colloidal solutions. The *ester*, $C_9H_{17}\cdot CO_2\cdot C_{10}H_{21}$, forms a colourless, mobile oil, b. p. 175—176°/11 mm., D_4^0 0·889, and D_4^{20} 0·868. It is hydrolysed by a cold concentrated solution of potassium hydroxide in methyl alcohol. Electrical conductivity measurements of the acid $C_{10}H_{20}O_2$, phytanic acid, and Δ^8-phytenic acid were made in aqueous alcoholic solution. The unsaturated acid is a better electrolyte than the saturated acid, and the acid $C_{10}H_{20}O_2$ conducts better than acetic acid.

A distillation flask similar to that described by Michael (Abstr., 1902, i, 70) is recommended for distillations under reduced pressure. Use is made of a column of glass beads, but the capillary tube for introducing bubbles of air is passed through a side-tube fused into the body of the flask. J. J. S.

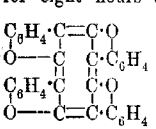
Condensation Products of 2-Coumaranone. KARL FRIES and W. PFAFFENDORF (*Ber.*, 1911, **44**, 114—124. Compare Abstr., 1910, i, 186; also Fries and Fink, Abstr., 1909, i, 42, 44).—By the condensation of 2-coumarone with sodium ethoxide solution in the absence of air, it has been found possible to obtain two isomeric compounds, $C_{16}H_{10}O_3$. The relative amounts of the two vary with the conditions, but so far it has not been found possible to ascertain the conditions which determine the proportions. Neither compound appears to have the hydroxylic structure corresponding with the acetyl derivative already described (Abstr., 1910, i, 186), as they are both very sparingly soluble in alkalis. They are represented as isomeric ketones, and both yield 2 : 1′-diketo-$\Delta^{1,2}$-1 : 2′-dicoumaran ("oxindirubin," "1 : 2-bis-coumaran-indigo"), when mixed with a small amount of bromine in glacial acetic acid solution.

2-*Keto*-1 : 2′-*coumarancoumarone*, $C_6H_4\langle\begin{matrix}CO\\O\end{matrix}\rangle CH\cdot C\langle\begin{matrix}C_6H_4\\CH\end{matrix}\rangle O$, is the chief product obtained by condensing 2-coumaranone with a hot 3% sodium ethoxide solution, and is also formed by the hydrolysis of the acetate (*loc. cit.*). It crystallises from methyl alcohol in compact, colourless needles, m. p. 116°, and its solution in concentrated sulphuric acid has a yellowish-red colour with a strong yellowish-green fluorescence. Its solutions, especially in the presence of impurities, are

unstable. It yields a somewhat unstable *hydrobromide* in the form of light red needles, and with acetic anhydride and sodium acetate yields the acetate of the tautomeric hydroxy-compound.

The isomeric 2-*keto*-$\Delta^{1:2'}$-*dicoumaran*, $C_6H_4\langle\begin{matrix}CO\\O\end{matrix}\rangle C{:}C\langle\begin{matrix}C_6H_4\\CH_2\end{matrix}\rangle O$, is more readily solubie in acetone, and crystallises from methyl alcohol in brilliant coppery-red plates, m. p. 141°. It is decomposed when boiled for some time with methyl alcohol, yields a yellowish-red *hydrochloride*, and is most readily obtained by condensing 2-coumarone with glacial acetic acid saturated with hydrogen bromide.

When either of the ketones or the acetate, m. p. 106°, is heated for eight hours at 100° with a saturated solution of hydrogen chloride in glacial acetic acid, a *product*, $C_{32}H_{16}O_6$, is obtained, which crystallises from xylene in flesh-coloured needles. These are not molten at 340°, but sublime in reddish plates with a metallic lustre. The annexed formula is suggested. Nitric acid converts it into a deep black-coloured substance, the acetic acid solution of which has a reddish-violet colour.



By the condensation of 5-methylcoumaranone with sodium ethoxide, only one product is obtained, namely, 2-*keto*-5 : 5′-*dimethyl*-$\Delta^{1:2'}$-*dicoumaran*, $C_{18}H_{14}O_3$. This crystallises from alcohol in yellow prisms, m. p. 156° (when quickly heated), and is readily oxidised to 5 : 5′-dimethyl-leuco-oxindirubin. It undergoes decomposition when heated alone or with glacial acetic acid. The *product*, $C_{36}H_{24}O_4$, obtained by heating the acetate, m. p. 133° (*loc. cit.*), with a saturated solution of hydrogen chloride in glacial acetic acid, crystallises from xylene in pale red needles, which melt above 340°. When rubbed with a little nitric acid it yields a blue-black compound, which dissolves in glacial acetic acid to brilliant violet-blue coloured solutions.

2 : 1′-Dihydroxy-1 : 2′-dicoumarone ("leuco-oxindirubin") yields a *phenylhydrazone*, $C_{22}H_{16}O_3N_2$, which crystallises from glacial acetic acid in pale red needles, m. p. 179°, and when hydrolysed with hydrochloric acid yields oxindirubin.

The *acetyl* derivative of 2 : 1′-dihydroxy-1 : 2′-dicoumarone, $C_{18}H_{12}O_5$, crystallises in glistening plates, m. p. 198°; when hydrolysed with alkalis it yields the *leuco*-compound, but with hydrochloric acid yields oxindirubin.

The *phenylhydrazone* of 2 : 1′-dihydroxy-5 : 5′-dimethyl-1 : 2′-dicoumarone, $C_{21}H_{20}O_3N_2$, forms red needles, m. p. 163°. The *oxime*, $C_{18}H_{15}O_4N$, crystallises from methyl alcohol in yellow needles, m. p. 194°, and the *acetyl* derivative, $C_{20}H_{16}O_5$, in yellow prisms, m. p. 200°.

J. J. S.

Oxindigo [2 : 2-Diketo-$\Delta^{1:1'}$-dicoumaran]. KARL FRIES and A. HASSELBACH (*Ber.*, 1911, 44, 124—128).—So far it has not been found possible to obtain "oxindigo" by the alkaline oxidation of 2-coumaranone, or from halogen derivatives of coumaranone (compare Abstr., 1897, i, 424; 1901, i, 94; 1909, i, 44, 174).

Attempts to prepare the oxygen compound of the action of

ammonium sulphide on *p*-dimethylaminoanildiketocoumaran were also unsuccessful.

By the condensation of the anil derivative with 2-coumaranone in boiling xylene, a product, $C_{24}H_{20}O_4N_2$, is formed, and this, when hydrolysed by means of a mixture of glacial acetic and concentrated sulphuric acid at the ordinary temperature, yields amino-dimethylaniline and "oxindigo."

3-*Keto*-2-p-*dimethylaminoanilcoumaran*,

$$C_6H_4\langle\begin{matrix}CO\\O\end{matrix}\rangle C{:}N\cdot C_6H_4\cdot NMe_2,$$

prepared by the action of an alcoholic solution of 2-coumaranone on an alcoholic solution of *p*-nitrosodimethylaniline in the presence of 2*N*-sodium hydroxide solution at 3°, crystallises from benzene in large prisms with a blue-black lustre, or from alcohol in dark brown, glistening needles, m. p. 185°. It is hydrolysed by strong acids to *p*-aminodimethylaniline and *o*-hydroxyphenylglyoxylic acid.

The condensation *product*, $C_{24}H_{20}O_4N_2$, probably

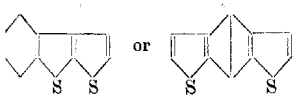
$$C_6H_4\langle\begin{matrix}CO\\O\end{matrix}\rangle C(NH\cdot C_6H_4\cdot NMe_2)\cdot CH\langle\begin{matrix}CO\\O\end{matrix}\rangle C_6H_4,$$

crystallises from a mixture of benzene and light petroleum in flat prisms with a bronzy lustre, m. p. 203° (decomp.), after sintering at 190°. The yield is 50% of the theoretical, and the product dissolves in alkali hydroxides, yielding reddish-brown solutions.

2 : 2-*Diketo*-$\Delta^{1:1'}$-*dicoumaran* ("*oxindigo*," "1 : 1-*dicoumarone-indigo*"), $C_6H_4\langle\begin{matrix}CO\\O\end{matrix}\rangle C{:}C\langle\begin{matrix}CO\\O\end{matrix}\rangle C_6H_4$, crystallises from glacial acetic acid or from xylene in long prisms, with an intense lemon-yellow colour. It has m. p. 272° after sintering at 250°, and its solution in concentrated sulphuric acid has a yellowish-red colour.

It is decomposed by alcoholic sodium hydroxide solution, and even by sodium carbonate in the presence of alcohol. J. J. S.

A New Thiophen Compound, $C_{10}H_6S_2$, and Some of its Derivatives. M. Lanfry (*Compt. rend.*, 1911, 152, 92—94).—The tarry product obtained when a mixture of sulphur and naphthalene vapour is passed through a red-hot iron tube contains 0·2—0·4% of a compound crystallising in ruby-red leaflets or clinorhombic prisms. The substance has m. p. 118·5° (corr.), b. p. 345°, and in composition approximates to the formula $C_{10}H_6S_2$; it is supposed to be *benzdithiophen* (annexed formulæ). It gives the thiophen reaction with sulphuric acid and isatin. The *bromo*-derivative, $C_{10}S_2H_2Br_4$, crystallises in silky, orange needles, m. p. 247—248°. The *tetranitro*-derivative, $C_{10}S_2H_2(NO_2)_4$, was obtained as an orange powder, decomposing at 300°; it has well-marked acid characters, and forms highly-coloured compounds with cyclic hydrocarbons.



On treating benzdithiophen with hydrogen peroxide in acetic acid solution, it yields in the first place a *compound*, $C_{10}H_6O_2S_2$, slender

rose-yellow needles, m. p. 130°, having the properties of a *p*-diphenol. On further oxidation, a second *compound*, $C_{10}H_6O_4S$, is formed; this crystallises in radiating, red needles, m. p. about 125°; it is insoluble in aqueous alkalis, and develops no coloration with sulphuric acid and isatin. W. O. W.

Silicotungstates of Coniceine, Sparteine, and Atropine. MAURICE JAVILLIER (*Bull. Sci. Pharm.*, 1910, 315—320. Compare Abstr., 1899, ii, 456; 1909, ii, 450).—*Coniceine silicotungstate*, $12WO_3,SiO_2,2H_2O,4C_8H_{17}N + 3H_2O$, prepared by adding potassium silicotungstate to an aqueous solution of coniceine tartrate, is an amorphous substance which becomes anhydrous at 120°. It is soluble in boiling water; 100 c.c. of water at 15° dissolve about 0·02 gram of the salt.

Sparteine silicotungstate, $12WO_3,SiO_2,2H_2O,2C_{15}H_{26}N_2 + 7H_2O$, is amorphous, and loses $6H_2O$ at 120°. The precipitation of this salt is visible in aqueous solutions containing 0·0002% of sparteine, and, consequently, may be employed in estimating the alkaloid.

Atropine silicotungstate, $12WO_3,SiO_2,2H_2O,4C_{17}H_{23}O_3N + 4H_2O$, becomes anhydrous at 120°. It is less easy to obtain pure than the foregoing, owing to a tendency to undergo hydrolysis. Advantage has been taken of its sparing solubility (less than 1 in 40,000) to estimate atropine in pharmaceutical preparations. W. O. W.

Preparation of Alkyl Halides and Alkyl Nitrates of Tropeine and Scopoleine Alkaloids. A. GERBER (D.R.-P. 228204).—*Methyl atropinium methosulphite*, $C_{17}H_{23}O_3NMe\cdot SO_3Me$, is prepared by heating atropine with methyl sulphite and methyl alcohol in a sealed tube at 100°; the *platinichloride*, $(C_{17}H_{23}O_3NMeCl)_2PtCl_4$, forms orange coloured leaflets. *Atropine methobromide*, m. p. 220°, and *atropine methonitrate* are formed respectively by evaporating the foregoing compound with aqueous potassium bromide, or with potassium nitrate; these compounds are soluble in water or alcohol, sparingly so in ether or acetone. F. M. G. M.

Dihydroberberine. JOHANNES GADAMER (*Arch. Pharm.*, 1910, 248, 670—681).—Faltis' evidence for the view that the action of potassium hydroxide on berberine results in the formation of oxyberberine and tetrahydroberberine (Abstr., 1910, i, 698) is reviewed and criticised, and further facts are brought forward in support of the author's opinion that in this reaction oxyberberine and dihydroberberine are formed (Abstr., 1902, i, 173, 555; 1905, i, 369; Freund and Beck, 1905, i, 151). Faltis' observation that by the action of zinc and acetic acid on oxyberberine, the latter is rendered colourless, could not be confirmed.

Dihydroberberine hydrochloride, prepared as already described (*loc. cit.*), crystallises with $4H_2O$, but readily loses $1H_2O$ on drying in a desiccator. Dihydroberberine is less basic than tetrahydroberberine, and is less easily removed than the latter from solution in ether by agitation with dilute hydrochloric acid. Tetrahydroberberine is resolved by crystallisation of the *d*-bromocamphorsulphonate into *d*- and *l*-canadines, but repetition of a similar fractional crystallisation

of dihydroberberine *d*-bromocamphorsulphonate (Abstr., 1902, i, 173) showed that no resolution of this base took place, although tetrahydroberberine was again easily resolved, either alone or in admixture with dihydroberberine.

Dihydroberberine furnishes a *methiodide*, m. p. 205°, which dissolves in water, forming a yellow solution giving no precipitate with ammonia, but forming a white precipitate with much sodium hydroxide, the liquid at the same time developing a violet fluorescence; the precipitate is not dissolved by ether. *Tetrahydroberberine methiodide*, m. p. 245—250°, is colourless and soluble with difficulty. Oxyberberine forms an additive product with methyl sulphate.

Dihydroberberine is more poisonous to rabbits than tetrahydroberberine. T. A. H.

Corydalis Alkaloids. V. *R*-Corydaline and Phenylberberine. Johannes Gadamer (*Arch. Pharm*, 1910, **248**, 681—695).—A description of direct and indirect attempts made to resolve optically inactive corydaline, m. p. 135°, into optically active forms (Abstr., 1902, i, 306; 1905, i, 463).

[With Ernst Steinbrecher.]—Attempts to effect resolution by fractionation of the tartrate, quinate, and *d*-bromocamphorsulphonate were unsuccessful. Natural *d*-corydaline does not give a crystalline salt with the last-mentioned acid.

Attempts were then made to effect the resolution of α-methyldihydroberberine (Freund and Beck, Abstr., 1905, i, 151), and to reduce the *d*- and *l*-isomerides thus obtained, so producing active forms, which should differ from corydaline only in containing a dioxymethylene group in place of two methoxyls, and should therefore correspond with the *d*- and *l*-corydalines and to *d*- and *l*-*meso*corydaline (compare Freund and Mayer, Abstr., 1907, i, 633). The resolution of *r*-α-methyldihydroberberine could not, however, be effected, and this was also the case for phenylberberine.

Oxyberberine treated with magnesium ethyl iodide in benzene solution, with dimethylaniline as a catalyst, was recovered for the most part unchanged, but small quantities of methylnoroxyberberine (Faltis, Abstr., 1910, i, 698) and of a non-basic *substance*, m. p. 165—166°, separating from alcohol in bright yellow crystals, were obtained.

Oxyberberine reacts with magnesium phenyl bromide in ether to form (1) a tertiary *base*, which may be either a phenyltetrahydroberberine or diphenyldihydroberberine, and (2) *phenylberberine*. The latter furnishes a *hydrochloride*, m. p. 255—257° (decomp.), which separates from alcohol or water in brownish-yellow crystals. The *aurichloride*, m. p. 215—216° (decomp.), forms long, brown needles from alcohol containing hydrochloric acid. The *acid sulphate* softens at 270°, but does not melt even at 278°, and separates from dilute sulphuric acid in compact, yellow crystals. The *nitrate*, m. p. 268—270° (decomp.), is deposited from alcohol in compact, brown crystals.

On reduction with zinc and dilute sulphuric acid, phenylberberine hydrochloride yields *phenyltetrahydroberberine*, m. p. 222°, which

separates from a mixture of chloroform and alcohol in compact, almost colourless crystals, and may also be obtained by reduction of phenyldihydroberberine. The latter, prepared by Freund and Beck's method (Abstr., 1905, i, 151), on oxidation with iodine in alcohol furnished *isophenylberberine*, which gives a *hydrochloride*, m. p. 275—278° (decomp.), separating from water in silky, bright yellow crystals. The *aurichloride* forms reddish-brown, short needles, sinters at 250°, but does not melt at 280°; along with it was produced a second gold salt, m. p. 223—225°, which may be impure phenylberberine aurichloride (see above), since on decomposition with hydrogen sulphide it yielded some phenylberberine hydrochloride. This phenylberberine is probably produced in the initial oxidation along with *iso*phenylberberine. The latter, on reduction, yielded a varnish from which no crystalline derivative could be obtained. The relationship between phenylberberine and *iso*phenylberberine is uncertain, and it is regarded as improbable that the difference is due to hydrogenation of a different pyridine nucleus in each case. T. A. H.

Preparation of Curarine. RUDOLF BOEHM (*Pflüger's Archiv*, 1910, 136, 203—207).—The action of curare is so uncertain, because commercial specimens contain other substances, in addition to its most active constituent curarine. The best kinds of curare contain only 3 to 9% of this alkaloid. Very small doses of curarine produce marked results. The methods of separating it from curare have been dealt with *in extenso* in the author's previous writings (Abstr., 1887, 1125; 1898, i, 283), and are briefly given in the present paper. W. D. H.

Preparation of Alkylhalogen Derivatives of Morphine Alkaloids. A. GERBER (D.R.-P. 228247).—The halogen double salts of the alkaloids and their quaternary compounds obtained by the action of alkyl halides and methyl sulphate have been previously described (Abstr., 1905, i, 542, 658; 1906, i, 530, 877; 1908, i, 452), and the work has now been extended to the products obtained with methyl sulphite.

Methylmorphinium methosulphite, $C_{17}H_{19}O_3NMe{\cdot}SO_3Me$, is prepared by heating morphine with methyl sulphite and methyl alcohol in a sealed tube at 100°, and subsequently evaporating in a vacuum; the amorphous, faintly coloured, hygroscopic product is rendered crystalline by dissolving in absolute alcohol and precipitating with ether; when evaporated with a saturated solution of potassium bromide, it is converted into morphine methobromide (m. p. 260°).

Methylnarcotinium methosulphite has similar properties, and is analogously prepared from narcotine; its *platinichloride*,

$$(C_{22}H_{23}O_7NMeCl)_2PtCl_4,$$

forms small, orange crystals.

Methylcodeinium methosulphite, *methylapomorphinium methosulphite*, *methylthebainium methosulphite*, with their respective *methobromides*, were also prepared; thebaine methobromide has m. p. 185°. F. M. G. M.

Strychnine and Brucine. II. ROBERTO CIUSA and G. SCAGLIARINI (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 501—505. Compare Abstr., 1910, *i*, 583).—When cacothelin is suspended in water acidified with hydrobromic acid and treated with bromine water until it has all dissolved, it is converted into the *hydrobromide* of an acid, $C_{19}H_{22}O_6N_2,HBr,2H_2O$, which is obtained in yellow crystals by the evaporation of the solution. The free acid, $C_{19}H_{22}O_6N_2,2H_2O$ (compare Hanssen, Abstr., 1887, 505), forms scales having a nacreous lustre. It is not toxic. The *platinichloride*, $(C_{19}H_{22}O_6N_2)_2,H_2PtCl_6$, obtained in presence of hydrochloric acid, crystallises in small, yellow prisms. R. V. S.

Identity of Vernine and Guanosine and Notes on Vicine and Convicine. ERNST SCHULZE and G. TRIER (*Zeitsch. physiol. Chem.*, 1910, **70**, 143—151. Compare Abstr., 1910, ii, 645).—The pentose (compare Schulze and Castoro, Abstr., 1904, ii, 506) obtained by the hydrolysis of vernine yields *l*-arabinose-*p*-bromophenylosazone (Levene and Jacobs, Abstr., 1909, i, 858), and is presumably *d*-ribose. A detailed comparison of vernine with Levene and Jacobs' guanosine (Abstr., 1910, i, 620) has proved that the two are identical.

The following formulæ are suggested for vicine and convicine, namely, $C_{20}H_{36}O_{15}N_8$ and $C_{20}H_{28}O_{16}N_6,2H_2O$.

The hydrolysis of vicine is represented by the equations:

$$(1)\ C_{20}H_{36}O_{15}N_8 + H_2O = \underset{\text{Divicin.}}{C_8H_{14}O_4N_8} + 2\underset{\text{Hexoses.}}{C_6H_{12}O_6}$$

$$(2)\ C_8H_{14}O_4N_8 + 4H_2O = C_8H_{10}O_8N_4 + 4NH_3,$$

and that of convicine by the equation:

$$C_{20}H_{28}O_{16}N_6,2H_2O + 4H_2O = \underset{\text{Alloxanthin.}}{C_8H_6O_8N_4,2H_2O} + 2C_6H_{12}O_6 + 2NH_3$$

(compare Ritthausen, Abstr., 1881, 1158; 1899, i, 715).

The two compounds are thus glucosides formed by the condensation of hexoses with pyrimidine derivatives. J. J. S.

Indole in Coal Tar. RUDOLF WEISSGERBER (*Ber.*, 1910, **43**, 3520—3528).—The *sodium* derivative of indole, $C_6H_4\langle\begin{matrix}CH\\NNa\end{matrix}\rangle CH$, is obtained in the form of a brown, amorphous mass, m. p. 140°, by heating indole with sodamide at 150—160°, or with sodium at 170—180°; it reacts with methyl iodide, yielding 1-methylindole, together with small quantities of 2-methylindole and 3-methylindole.

On warming with benzoyl chloride in benzene solution, it yields *benzoylindole*, $C_6H_4\langle\begin{matrix}CH\\NBz\end{matrix}\rangle CH$; the latter crystallises from alcohol in compact, rhombic plates, m. p. 67—68°, b. p. 213°/16 mm., and is readily hydrolysed by aqueous sodium hydroxide.

The *potassium* derivative of indole is obtained as a light-coloured mass by heating indole with potassium hydroxide.

The formation of the potassium compound furnishes a ready means of separating indole from coal tar. The fraction, b. p. 240—260°, freed from phenols and bases by shaking with alkali hydroxide and dilute sulphuric acid is heated with potassium hydroxide at 190—200°,

the unattacked oil removed by washing with benzene, and the potassium indole decomposed by water; the separation may also be effected by means of sodium or sodamide.

The crude indole may be purified by converting it into the bisulphite compound (Hesse, Abstr., 1900, i, 48), or into the sodium salt of indolecarboxylic acid (compare Zatti and Ferratini, Abstr., 1890, i, 292), by heating with sodium at 190—200° in a stream of carbon dioxide. The free acid obtained from the sodium salt by acidification loses carbon dioxide when heated in a vacuum at 230—250° and yields indole. F. B.

Preparation of Halogenindoxylic Acids and their Esters. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 226689).—The conversion by alkalis of phenylglycine-*o*-carboxylic acids into derivatives of indoxyl has been described (compare Abstr., 1908, i, 974, 1019), and it is now found that the reaction can be applied successfully to halogenated derivatives of the acid.

Methyl 5 : 7-*dichloroindoxylcarboxylate*, $C_6H_2Cl\langle^{-NH-}_{C(OH)}\rangle C\cdot CO_2Me$, colourless needles, m. p. 195°, is prepared by boiling *dimethyl* 4 : 6-*dichlorophenylglycine*-2-*carboxylate*, m. p. 77—78°, in toluene solution with sodium or sodium methoxide; the toluene can be replaced by other indifferent solvents.

Dimethyl 6-*chloro*-4-*bromophenylglycine*-2-*carboxylate*, m. p. 81—83° (obtained from 6-chloro-4-bromophenylglycine-2-carboxylic acid, m. p. 238°, in the usual manner), yielded on similar treatment *methyl* 7-*chloro*-5-*bromoindoxylcarboxylate*, $C_6H_2ClBr\langle^{-NH-}_{C(OH)}\rangle C\cdot CO_2Me$, long needles, m. p. 203—205°.

Methyl 4 : 6-*dichlorophenylglycine*-2-*carboxylate*, colourless needles, m. p. 133—134°, on treatment with sodium ethoxide yielded *sodium* 5 : 7-*dichloroindoxylcarboxylate*, a yellow powder which is readily converted into 5 : 7 : 5′ : 7′-tetrachloroindigotin by the action of air and water. F. M. G. M.

Betaine Formation and Steric Hindrance. ALFRED KIRPAL (*Monatsh.*, 1910, **31**, 969—979. Compare Abstr., 1908, i, 679).—Nicotinic, *iso*nicotinic, and cinchomeronic acids interact with chloroacetic acid in neutral solution, giving almost theoretical yields of the corresponding betaines; picolinic and quinolinic acids, under the same conditions, react incompletely, whilst dipicolinic acid remains unchanged. The author suggests that these results may be explained on the assumption that the carboxyl group in the α-position exerts a negative influence on the nitrogen atom, which therefore shows less tendency to assume the quinquevalent condition. This explanation is, however, not applicable to quinaldine and 2 : 6-dimethylpyridine, both of which, on treatment with chloroacetic acid, do not yield betaine, but are converted into their hydrochlorides; the non-formation of betaines in these cases is referred to steric influences.

iso.Nicotinic acid betaine, $C_8H_7O_4N$, prepared by heating *iso*nicotinic

acid and chloroacetic acid in faintly alkaline, aqueous solution, crystallises in needles, m. p. 262° (decomp.).

Nicotinic acid betaine forms monoclinic prisms or octahedral crystals, and has m. p. 190° (decomp.).

Picolinic acid betaine crystallises in short, pointed prisms, m. p. 165° (decomp.); the *hydrochloride* has m. p. 181°.

Cinchomeronic acid betaine, $C_9H_7O_6N$, forms rhombic plates, m. p. 180° (decomp.).

Quinolinic acid betaine, $C_9H_7O_6N,H_2O$, crystallises in colourless prisms, which, when heated at 100°, lose their water of crystallisation and carbon dioxide, yielding nicotinic acid betaine; the same decomposition also takes place on boiling its aqueous solution; the *hydrochloride* is readily hydrolysed, aqueous solutions rapidly depositing the free betaine.

α-Picolinebetaine, $C_8H_9O_2N$, prepared by heating α-picoline with chloroacetic acid on the water-bath and isolated by means of its platinichloride, crystallises in colourless, hygroscopic needles, which turn brown at 100° and decompose at 162°; the *platinichloride* forms yellow prisms, m. p. 212° (decomp.); the *hydrochloride* has m. p. 188° (decomp.). F. B.

Derivatives of 2-Phenylquinoline. II. Ernst Murmann (*Monatsh.*, 1910, **31**, 1303—1306. Compare Abstr., 1892, 1003).—Disulphonic acids can be obtained by heating 1-phenylquinoline with four times its weight of commercial fuming sulphuric acid on the water-bath until a test drop gives no crystals (monosulphonic acid) when heated with five drops of water and no turbidity on addition of aqueous ammonia.

The mass is diluted with five times its weight of water, and a small amount of monosulphonic acid separates during the course of a day. After further dilution, boiling with animal charcoal, and neutralising with barium carbonate, crystals of a *barium* salt,

$$C_{15}H_9O_6NS_2Ba,6H_2O,$$

in the form of long, colourless needles, are obtained. The *calcium* salt, $C_{15}H_9O_6NS_2Ca,6H_2O$, forms slender, yellow needles, sparingly soluble in water, and the *zinc* salt crystallises with $5H_2O$ in large, felted needles.

The filtrate from the barium salt contains an isomeric salt, which is sparingly soluble in alcohol, and crystallises with $12H_2O$. The first barium salt, when fused with potassium hydroxide, yields a red *phenol*, m. p. 140—141°. J. J. S.

Formation of Acyl Derivatives of Phenylhydrazine in Aqueous Solution. Stephan Jaroschy (*Monatsh.*, 1910, **31**, 951—967).—The phenylhydrazides of formic, acetic, propionic, butyric, and *iso*butyric acids are readily formed by heating the acids with phenylhydrazine in aqueous solution. The relative velocities of formation of these hydrazides under various conditions at 100° have been investigated by estimating the amount of unchanged acid by titration with barium hydroxide. With the same concentration of acid

and of base, it is found that the rates of formation stand in the same order as the magnitude of the dissociation constants of the acids.

The effect of temperature was studied in the case of the formyl derivative. Increase of temperature is accompanied by an increase in the relative velocity, and the same effect is produced by increasing the concentration of the acid.

The addition of a small quantity of hydrochloric acid was found to diminish the rate of formation of the acetyl derivative. The author suggests that this is to be referred to the diminution in the ionisation of the acetic acid; on this assumption, the acylation is due to the anions. F. B.

Oxidation of Methyluracil. Robert Behrend and Karl Steuve (*Annalen*, 1910, 378, 153—169. Compare Behrend and Dietrich, Abstr., 1900, i, 120; Behrend and Grünewald, Abstr., 1902, i, 834; Behrend and Fricke, Abstr., 1903, i, 739; Behrend and Osten, Abstr., 1906, i, 309; Behrend and Hufschmidt, Abstr., 1906, i, 310; Hobel, Abstr., 1907, i, 557; Offe, *ibid.*, 645).—When oxidised with potassium ferricyanide in ammoniacal solution, methyluracil yields the amide of uracilcarboxylic acid: $CO<^{NH—CO}_{NH\cdot CMe}>CH + NH_3 + 3O =$ $CO<^{NH————CO}_{NH\cdot C(CO\cdot NH_2)}>CH + 2H_2O$. This appears to be the first instance recorded of the oxidation of a $-CH_3$ to a $-CO\cdot NH_2$ group. The reaction does not consist in the oxidation of the methyl to a carboxylic group and the conversion of the latter into the $-CO\cdot NH_2$ group by means of ammonia, as it is shown that a temperature of 240° is required for the latter reaction. It is possible that an aldehyde group is first formed, and that this yields an aldehyde-ammonia, $-CH<^{OH}_{NH_2}$, which is then oxidised to the $-CH<^{O}_{NH_2}$ group. When the oxidation takes place in the presence of potassium hydroxide the product is uracilcarboxylic acid.

In the preparation of the amide, the mixture is heated at 50—60° for five to six hours and allowed to cool, when potassium ferrocyanide separates; this is removed, and the filtrate heated until all the ammonia is driven off and an odour of hydrogen cyanide is noticed. The solution is filtered hot and kept for one to two days at the ordinary temperature, when methyluracil separates as octahedra or needles, and in the course of a week or so the amide separates in a crystalline form. It is most readily freed from uracil by conversion into its sparingly soluble *potassium* derivative, $C_5H_4O_3N_3K,2H_2O$, which crystallises from hot water in well-developed prisms. Its solution has an alkaline reaction. The *amide*, $C_5H_5O_3N_3,H_2O$, crystallises in small, lancet-shaped plates, dissolves in 110 parts of boiling water, and in 2000 parts of water at 20°. When boiled with alkalis, it yields *uracil-carboxylic acid*, $CO<^{NH————CO}_{NH\cdot C(CO_2H)}>CH,H_2O$, in the form of rhombic plates which lose their water of hydration at 120°. The anhydrous compound decomposes above 300° without melting. The hydrated compound dissolves in 70 parts of water at 100° and in 500 parts at 18°.

The addition of acetic acid to a solution of the carboxylic acid in potassium hydroxide solution precipitates *potassium uracilcarboxylate*, $C_5H_3O_4N_2K$. The *ammonium* salt, $C_5H_7O_4N_3,H_2O$, crystallises in small, six-sided plates. The acid is identical with the product obtained by hydrolysing the ester described by Müller (Abstr., 1897, i, 549).

When methyluracil is oxidised with potassium ferricyanide in the presence of potassium hydroxide solution, it is best to leave the mixture for twenty days at the ordinary temperature and then to acidify with acetic acid, when potassium uracilcarboxylate is precipitated.

It has not been found possible to oxidise the carboxylic acid with potassium ferricyanide, but with permanganate (3O) at 15° the acid yields oxaluric and oxalic acids. J. J. S.

Oxidation of α- and β-Dimethyluracils. Paul Henkel (*Annalen*, 1910, 378, 170—187. Compare Behrend and Grünewald, Abstr., 1902, i, 834).—The oxidation of α- and β-dimethyluracils is analogous to that of methyluracil (compare table given by Osten, *Annalen*, 1905, 343, 151). Methylparabanic acid can be isolated from the oxidation products of both compounds, under conditions such that its formation from methyloxaluric acid is excluded. The two dimethyluracils have been transformed into corresponding α- and β-trihydroxydimethyldihydrouracils by Osten's method (Abstr., 1906, i, 309). These hydroxy-derivatives exist in only one form, whereas the corresponding trihydroxymethyldihydrouracil exists in two forms (Abstr., 1908, i, 840). Although it has not been found possible to isolate an acetylmethylallanturic acid by the action of alkali on the trihydroxy-derivatives, it is shown that a conversion of the six-membered ring into a five-membered ring must take place under the influence of alkalis, since, when oxidised with permanganate in the presence of excess of potassium hydrogen carbonate, the α-trihydroxy-derivative yields methylparabanic acid together with methyloxaluric acid, but no trace of acetylmethylcarbamide. Trihydroxy-β-dimethyldihydrouracil is oxidised much less readily, and under similar conditions yields *s*-acetylmethylcarbamide together with methyloxaluric acid and methylparabanic acid; but when the solution of the hydroxy-compound is left in contact with the potassium hydrogen carbonate for twenty-four hours before the addition of the permanganate, the products obtained are methylparabanic acid and methyloxaluric acid. Acetylmethyloxaluric acid is not formed during the oxidation in the presence of the carbonate.

Nitro-α-dimethyluracil (*5-nitro-2:6-dioxy-3:4-dimethyldihydropyrimidine*), $CO<^{NH\text{---}CO}_{NMe\cdot CMe}>C\cdot NO_2$, prepared by Osten's method (*loc. cit.*), crystallises from water in yellow plates, m. p. 249—250°, and when reduced by Behrend and Grünewald's method (*loc. cit.*) yields the corresponding *amino*-derivative, $C_6H_9O_2N_3$, in the form of yellow crystals, m. p. 281—282°.

Trihydroxy-α-dimethyldihydrouracil (*4:5:5-trihydroxy-2:6-dioxy-3:4-dimethyldihydropyrimidine*), $CO<^{NH\text{---------}CO}_{NMe\cdot CMe(OH)}>C(OH)_2$, obtained by oxidising the amino-α-dimethyluracil with bromine water at low temperatures, crystallises when its aqueous solution is concentrated

at the ordinary temperature under 4 mm. pressure, and decomposes at 120°. When heated at 70—80° for fifteen minutes with ethyl alcohol, it yields the 5 : 5-*diethoxy*-derivative, $CO<^{NH\text{———}CO}_{NMe\cdot CMe(OH)}>C(OEt)_2$, which crystallises from alcohol, and has m. p. 114—116°.

Nitro-β-dimethyluracil (*5-nitro-2 : 6-dioxy-1 : 4-dimethyldihydropyrimidine*), $CO<^{NMe\text{—}CO}_{NH\cdot CMe}>C\cdot NO_2$, crystallises from water in pale yellow prisms, m. p. 229—230° (decomp.); the corresponding *amino*-derivative has m. p. 256—257° (decomp.), and *trihydroxy-β-dimethyldihydrouracil* (*4 : 5 : 5-trihydroxy-2 : 6-dioxy-1 : 4-dimethyldihydropyrimidine*), $CO<^{NMe\text{———}CO}_{NH\cdot CMe(OH)}>C(OH)_2$, crystallises from dilute acetic acid, and decomposes at 133°.

Bromo-β-dimethyluracil, $CO<^{NMe\cdot CO}_{NH\cdot CMe}>CBr$, is sometimes formed as a by-product; it has m. p. 243°. *4-Hydroxy-5 : 5-diethoxy-2 : 6-dioxy-1 : 4-dimethyldihydropyrimidine*, $C_{10}H_{18}O_5N_2$, crystallises from alcohol, has m. p. 124—126° (decomp.), and dissolves in 20 parts of cold absolute alcohol.

Methylparabanic acid is readily transformed into methyloxaluric acid when its alcoholic solution is made alkaline with *N*/5 alcoholic potash and kept for an hour.

It has not been found possible to obtain either of the above-mentioned nitro-derivatives by the action of methyl iodide and alkali on nitromethyluracil. J. J. S.

Action of Potassium Permanganate and of Bromine on 1 : 4 : 5-Trimethyluracil. KARL BREMER (*Annalen*, 1910, 378, 188—209).—By analogy with methyluracil (Abstr., 1906, i, 310) it was thought probable that by the oxidation of 1 : 4 : 5-trimethyluracil with cold permanganate, methylacetylcarbamide and pyruvic acid would be formed, and that with warm permanganate, acetyldimethylhydantoin or its oxidation products would be obtained. Actual experiment has shown that the products are the same at both temperatures, using 2 atoms of oxygen; in both cases, only acetylmethylcarbamide and a syrup are formed. No trace of pyruvic acid can be detected in the syrup, and the only product so far isolated from the syrup is oxalic acid. Dihydroxytrimethyldihydrouracil has been prepared by Behrend, Osten, and Beer's method (Abstr., 1906, i, 309), but it has not been settled definitely whether the compound has the constitution of the uracil (1) or whether it is the isomeric acetyldimethyl hydantoin (2).

(1) $CO<^{NMe\text{———}CO}_{NH\cdot CMe(OH)}>CMe\cdot OH$. (2) $CO<^{NMe\cdot CO}_{NH\text{—}CMe\cdot CMe(OH)_2}$

In favour of the latter formula are the facts that it is not readily oxidised, and does not appear to be affected by alkalis.

Attempts to oxidise 1-phenyl-4 : 5-dimethyluracil were unsuccessful, owing to the slight solubility of the compound in water.

Behrend and Hennicke's method (Abstr., 1906, i, 314) for the preparation of thiontrimethyluracil gives a 25% and not an 80% yield. A 45—50% yield is obtained when a mixture of equivalent

quantities of methyl thiocarbimide and ethyl β-amino-α-methyl crotonate is heated to 55—60° and then kept for twenty-four hours in an ice chest; after removing the crystals, the filtrate is heated to 70°, and on cooling gives a further crop of crystals. The desulphurisation is accomplished most readily by heating the compound in a reflux apparatus with 65% sulphuric acid for about forty-five minutes at 150—160° and subsequent dilution with three times the volume of water. The yield of trimethyluracil is 80%; it crystallises from hot water, and has m. p. 222—223°.

1-Phenyl-4 : 5-dimethyluracil, $C_{12}H_{12}O_2N_2$, is formed when ethyl phenylcarbamidomethylcrotonate (Abstr., 1901, i, 136), prepared from ethyl β-amino-α-methylcrotonate and phenylcarbimide, is hydrolysed with 5% potassium hydroxide solution and the solution acidified with hydrochloric acid; it has m. p. 235°.

4-*Bromo*-5-*hydroxy*-1 : 4 : 5-*trimethyldihydrouracil*,

$$CO<^{NMe\text{---}CO}_{NH\cdot CMeBr}>CMe\cdot OH,$$

obtained by the action of water and an excess of bromine on trimethyluracil at the temperature of the water-bath, crystallises from hot water in needles, m. p. 127° after sintering at 120°. When heated with alcohol, or by itself at 95°, and then at 115°, it loses water and yields 4-*bromo*-1 : 4-*dimethyl*-5-*methylenedihydrouracil*,

$$CO<^{NMe\text{---}CO}_{NH\cdot CMeBr}>C:CH_2,$$

which crystallises from benzene or dilute alcohol, and has m. p. 195° after sintering at 170°. This unsaturated compound reacts with bromine water, yielding 4-*bromo*-5-*hydroxy*-1 : 4-*dimethyl*-5-*bromomethyldihydrouracil*, $CO<^{NMe\text{---}CO}_{NH\cdot CMeBr}>C(CH_2Br)\cdot OH$, m. p. 150—151° after sintering at 145°, and this, when heated at 90—100° for three hours, yields 4-*bromo*-1 : 4-*dimethyl*-5-*bromomethylenedihydrouracil*, $CO<^{NMe\text{---}CO}_{NH\cdot CMeBr}>C:CHBr$, in the form of well-developed needles, m. p. 175—178°, which again react with bromine water, yielding 4-*bromo*-5-*hydroxy*-1 : 4-*dimethyl*-5-*dibromomethyldihydrouracil*, $CO<^{NMe\text{---}CO}_{NH\cdot CMeBr}>C(CHBr_2)\cdot OH$, as colourless crystals.

Dibromohydroxymethyldihydrouracil does not yield an unsaturated compound when heated at 150°.

Chlorohydroxytrimethyldihydrouracil, $C_7H_{11}O_3N_2Cl$, obtained by the action of chlorine water on trimethyluracil, crystallises from hot water, and has m. p. 154—155°.

4-*Bromo*-5-*hydroxy*-1-*phenyl*-4 : 5-*dimethyldihydrouracil*,

$$C_{12}H_{13}O_3N_2Br,$$

has m. p. 195°.

4 : 5-*Dihydroxy*-1 : 4 : 5-*trimethyldihydrouracil*, $C_7H_{12}O_4N_2$, prepared from the bromohydroxy-compound by Behrend and Grünewald's method, crystallises from water in large prisms, m. p. 165°. It reacts with boiling acetic anhydride, yielding an *acetyl* derivative, $C_9H_{14}O_5N_2$, m. p. 135—150°, and with phenyldydrazine yields a *phenylhydrazide*, $C_{18}H_{18}O_3N_4$, in the form of needles, m. p. 155—158° after sintering at 145°.

J. J. S.

Quinazolines. XXVI. Synthesis of Some Stilbazoles, Hydrazones, and Schiff Bases in the 4-Quinazolone Group. MARSTON T. BOGERT, GEORGE DENTON BELL, and CARL GUSTAVE AMEND (*J. Amer. Chem. Soc.*, 1910, **32**, 1654—1664).—It has been shown in earlier papers (Bogert and Gortner, Abstr., 1909, i, 679; Bogert, Amend, and Chambers, Abstr., 1910, i, 893) that derivatives of 4-quinazolone can be easily prepared which contain a 2-methyl group and amino-groups attached to either or both the benzene and metadiazine portions of the nucleus. A study has been made of the behaviour of these different groups towards aldehydes, and the results show that with reference to their reactivity with benzaldehyde they may be arranged in the following order: (1) the 3-amino-group (in the metadiazine nucleus); (2) the 2-methyl-group; and (3) the 7-amino-group (in the benzene nucleus).

When 2-methyl-4-quinazolone is boiled for ten minutes with benzaldehyde, it is converted into the stilbazole, namely, 2-*styryl*-4-*quinazolone* (2-*styryl*-4-*hydroxyquinazoline*), $C_6H_4<^{N=C\cdot CH:CHPh}_{CO\cdot NH}$ or $C_6H_4<^{N=\!=C\cdot CH:CHPh}_{C(OH):N}$, m. p. 252—253° (corr.), which forms colourless, silky needles, and yields a *bromo*-derivative. 2-*o*-*Hydroxystyryl*-4-*quinazolone*, $C_6H_4<^{N=C\cdot CH:CH\cdot C_6H_4\cdot OH}_{CO\cdot NH}$, m. p. 307° (decomp.), obtained by the action of salicylaldehyde on 2-methyl-4-quinazolone, crystallises in minute, pale yellow needles, and yields bright yellow *salts* with hydrochloric acid and potassium hydroxide. 2-*p*-*Hydroxy*-*m*-*methoxystyryl*-4-*quinazolone*, $C_6H_4<^{N=C\cdot CH:CH\cdot C_6H_3(OH)\cdot OMe}_{CO\cdot NH}$, m. p. 280° (corr.), forms minute, pale yellow needles and gives dark yellow alkali salts.

When 2 : 3-dimethyl-4-quinazolone is boiled with benzaldehyde, 2-*styryl*-3-*methyl*-4-*quinazolone*, $C_6H_4<^{N=C\cdot CH:CHPh}_{CO\cdot NMe}$, m. p. 170° (corr.), is produced, which forms light yellow, slender needles.

3-Amino-2-methyl-4-quinazolone was prepared by the action of hydrazine hydrate on acetylanthranil (Bogert and Gortner, *loc. cit.*). In one experiment, a compound, m. p. 193° (corr.), was isolated, which crystallises in prisms, and is probably *acetylanthranylacetylhydrazide*, $NHAc\cdot C_6H_4\cdot CO\cdot NH\cdot NHAc$. The hydrazone, 3-benzylideneamino-2-methyl-4-quinazolone, obtained by boiling 3-amino-2-methyl-4-quinazolone (1 mol.) with benzaldehyde (1 mol.), has m. p. 187° (corr.), and not 183° as stated by Bogert and Gortner (*loc. cit.*); its *hydrochloride* softens at 220°, and decomposes without melting at about 300°. When 3-amino-2-methyl-4-quinazolone (1 mol.) is boiled with benzaldehyde (2 mols.), 3-*benzylideneamino*-2-*styryl*-4-*quinazolone*,

$$C_6H_4<^{N=C\cdot CH:CHPh}_{CO\cdot N\cdot N:CHPh},$$

m. p. 155° (corr.), is obtained, which forms minute, nearly colourless, stellate groups of crystals; its *hydrochloride* does not melt below 300°. When this substance is treated with boiling dilute hydrochloric acid

and the product distilled with steam, benzaldehyde passes over with the distillate, and 3-*amino*-2-*styryl*-4-*quinazolone*,

$$C_6H_4\begin{cases}N{=}C\cdot CH{:}CHPh\\ CO\cdot N\cdot NH_2\end{cases}$$

m. p. 164° (corr.), is obtained, which crystallises in plates or broad needles, and when heated with benzaldehyde is reconverted into its benzylidene derivative; the *benzoyl* derivative has m. p. 195° (corr.). When 3-amino-2-methyl-4-quinazolone is heated with cinnamaldehyde, salicylaldehyde, or vanillaldehyde, the methyl group is not affected, but condensation takes place only with the amino-group. 3-*Cinnamylideneamino*-2-*methyl*-4-*quinazolone*, m. p. 148—149° (corr.), forms bright yellow needles. The corresponding *salicylidene* derivative, m. p. 171° (corr.), crystallises in short, pale yellow needles, yields a bright yellow *potassium* salt and a *hydrochloride*, m. p. 250° (decomp.), and is hydrolysed by hydrochloric acid or potassium hydroxide with formation of salicylaldehyde. Although the salicylidene compound refuses to condense with a second mol. of salicylaldehyde, it condenses readily with benzaldehyde with formation of 3-*salicylideneamino*-2-*styryl*-4-*quinazolone*, $C_6H_4\begin{cases}N{=}C\cdot CH{:}CHPh\\ CO\cdot N\cdot N{:}CH\cdot C_6H_4\cdot OH\end{cases}$, m. p. 232—233° (corr.), which crystallises in yellow needles. 3-*Vanillylideneamino*-2-*methyl*-4-*quinazolone*, m. p. 215—216° (corr.), forms small, yellow prisms or needles, and gives deep, yellow salts with hydrochloric acid and potassium hydroxide.

In the case of 7-amino-2-methyl-4-quinazolone, as in that of the 3-amino-derivative, condensation is possible with either the methyl or amino-group or with both. The amino-group, however, is differently situated, being in the benzene instead of the metadiazine nucleus and attached to a carbon instead of a nitrogen atom. Aldehydes condensing with the 7-amino-group should therefore yield true Schiff bases instead of hydrazones. In one experiment, a *benzylidene* derivative, m. p. 324° (corr.), was obtained, which seemed to be the Schiff base, since it was hydrolysed by potassium hydroxide with formation of benzaldehyde and the quinazolone, but this compound could not be obtained subsequently; its *acetyl* derivative has m. p. 274—276° (corr.). 7-*Acetylamino*-2-*styryl*-4-*quinazolone*,

$$NHAc\cdot C_6H_3\begin{cases}N{=}C\cdot CH{:}CHPh,\\ CO\cdot NH\end{cases}$$

m. p. 323—324° (corr.), obtained by boiling 7-acetylamino-2-methyl-4-quinazolone with benzaldehyde, forms short, colourless needles.

7-Amino-2:3-dimethyl-4-quinazolone condenses with benzaldehyde to form 7-*amino*-2-*styryl*-3-*methyl*-4-*quinazolone*,

$$NH_2\cdot C_6H_3\begin{cases}N{=}C\cdot CH{:}CHPh\\ CO\cdot NMe\end{cases}$$

m. p. 229·5—230° (corr.), which crystallises in yellow prisms; its *acetyl* derivative has m. p. 272° (corr.).

When 3:7-diamino-2-methyl-4-quinazolone is boiled with an excess of benzaldehyde, 3:7-*dibenzylideneamino*-2-*styryl*-4-*quinazolone*,

$$CHPh{:}N\cdot C_6H_3\begin{cases}N{=}C\cdot CH{:}CHPh\\ CO\cdot N\cdot N{:}CHPh\end{cases}$$

m. p. 238° (corr.), is produced, together with small quantities of two

other *substances*, m. p. 196° (corr.) and 172° (corr.), which seem to be isomeric dibenzylidene derivatives. *7-Acetylamino-3-benzylideneamino-2-styryl-4-quinazolone*, m. p. 261° (corr.), obtained by boiling 3-amino-7-acetylamino-2-methyl-4-quinazolone with excess of benzaldehyde, forms yellow needles; its solution in alcohol has a green fluorescence. 3 : 7-Diacetylamino-2-methyl-4-quinazolone condenses with benzaldehyde with formation of 3 : 7-*diacetylamino-2-styryl-4-quinazolone*, m. p. 283—284° (corr.).

3-Amino-6-acetylamino-2-methyl-4-quinazolone condenses similarly with benzaldehyde with production of 6-*acetylamino-3-benzylideneamino-2-styryl-4-quinazolone*, m. p. 238—239° (corr.), which forms short, silky, yellow needles. E. G.

Constitution of Indirubin. I. and II. ANDRÉ WAHL and P. BAGARD (*Bull. Soc. chim.*, 1910, [iv], 7, 1090—1101; 1911, 9, 56—83. Compare Abstr., 1909, *i*, 330, 735).—I. Maillard's objection (Abstr., 1910, i, 138) to the view that the authors' new synthesis of indirubin (Abstr., 1909, i, 330) supports von Baeyer's formula for this substance is based on two main contentions: (*a*) that proof of the formation of indirubin was insufficient; (*b*) that molecular transformation may have occurred in the reaction.

In regard to (*a*) it is now shown that the synthetic indirubin, like commercial indirubin, yields Schunk and Marchlewski's colourless, crystalline compound, m. p. 204°, when reduced with zinc and acetic anhydride in presence of anhydrous sodium acetate (Abstr., 1893, i, 288). Contention (*b*) implies that both oxindole and indoxyl should condense with isatin chloride to give indirubin, but actual trial shows that when the reaction is conducted in presence of pyridine to remove the hydrogen chloride formed, indoxyl gives indigotin and no indirubin, whereas oxindole gives indirubin as chief product.

II. *m*-Bromoisatin chloride condenses with oxindole to furnish a bromoindirubin, which is isomeric with, but different from, that obtained by condensing *m*-bromoisatin with indoxylic acid. The production of isomerides in these two reactions can be explained easily from von Baeyer's, but only with difficulty from Maillard's, formula.

m-Bromoisatin chloride condenses with oxindole in benzene solution to form a *bromoindirubin*, having the formula

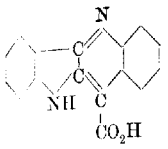
$$NH\langle\begin{matrix}C_6H_4\\CO\end{matrix}\rangle C{:}C\langle\begin{matrix}CO\\NH\end{matrix}\rangle C_6H_3Br.$$

It forms dichroic, triclinic crystals, showing oblique extinction and angle $ph' = 126°$. Its solubility is 0·192—0·199 gram in 100 grams of acetic acid at 25°. The bromoindirubin obtained by condensing *m*-bromoisatin with indoxylic acid has the formula

$$C_6H_4\langle\begin{matrix}NH\\CO\end{matrix}\rangle C{:}C\langle\begin{matrix}C_6H_3Br\\CO\end{matrix}\rangle NH,$$

and has been prepared already by von Baeyer (Abstr., 1882, 198). It forms dichroic crystals which belong to the monoclinic system, and show right extinction and angle $ph' = 101°$. Its solubility is 0·042—0·052 gram in 100 grams of acetic acid at 25°. T. A. H.

Quindoline and "Thioquindoline." EMILIO NOELTING and O. R. STEUER (*Ber.*, 1910, **43**, 3512—3517).—Indoxylic acid condenses with *o*-aminobenzaldehyde in hydrochloric acid solution, yielding quindoline



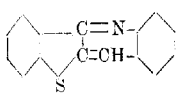
(compare Fichter and Böhringer, Abstr., 1907, i, 92; Fichter and Rohner, this vol., i, 85). This is identical with indoline described by Schützenberger (this Journ., 1877, ii, 898).

By heating indigotin with an alkaline solution of sodium thiosulphate, Geraud (Abstr., 1879, 936; 1881, 51) obtained a substance to which he assigned the formula $C_{32}H_{24}O_3N_4$. Since the same compound is also produced by the condensation of indoxyl and isatin in alkaline solution, it must be a *quindolinecarboxylic acid* of the annexed structure.

2-o-Nitrobenzylidene-indoxyl, $C_6H_4<^{CO-}_{NH}>C{:}CH{\cdot}C_6H_4{\cdot}NO_2$, prepared by the condensation of *o*-nitrobenzaldehyde and indoxylic acid in aqueous acetic acid solution, crystallises in red needles, m. p. 217°; on reduction with zinc dust and acetic acid it yields quindoline.

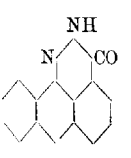
By condensing indoxylic acid with *o*-aminobenzaldehyde in the presence of a little hydrochloric acid, *2-o-aminobenzylidene-indoxyl*, $C_6H_4<^{CO-}_{NH}>C{:}CH{\cdot}C_6H_4{\cdot}NH_2$, is produced; if the condensation is carried out in more acid solution, quindoline hydrochloride is obtained.

3-Keto-2-o-nitrobenzylidene-thionaphthen, $C_6H_4<^{CO-}_{S-}>C{:}CH{\cdot}C_6H_4{\cdot}NO_2$, prepared from *o*-nitrobenzaldehyde and 3-hydroxythionaphthen-2-carboxylic acid in acetic acid solution, crystallises from alcohol in orange-yellow needles, m. p. 171°; on reduction it yields "*thioquindoline*" (annexed formula). The latter crystallises in almost colourless needles, m. p. 169°, and with concentrated acids forms yellow salts, which are decomposed by water; the *hydrochloride* and *picrate* are described.

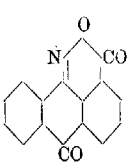


Quindoline and "thioquindoline" dye tannin-mordanted wool, silk, and cotton pale yellow; with quindolinecarboxylic acid the shade is somewhat deeper. F. B.

Anthraquinone-1-carboxylic Acid. FRITZ ULLMANN and WILLEM VAN DER SCHALK (*Ber.*, 1911, **44**, 128—129).—*Anhydro-anthraquinone-9-hydrazone-1-carboxylic acid* (*pyridazonanthrone*) (I), obtained by the action of hydrazine hydrate on the chloride of anthraquinone-1-carboxylic acid, crystallises in needles which are sparingly soluble in the usual solvents, but dissolve in sodium hydroxide to orange-yellow solutions. Phenylhydrazine gives the corresponding *N*-phenylpyridazonanthrone. Anthraquinone-1-carb-



(I.)



(II.)

oxylic acid reacts readily with hydroxylamine in the presence of sodium acetate solution, yielding *oxazonanthrone* (II) in the form of pale yellow needles, m. p. 247°. J. J. S.

Method for Preparing Aromatic Acylguanidines. PAUL PIERRON (*Compt. rend.*, 1910, **151**, 1364—1366. Compare Wheeler and Johnson, Abstr., 1902, i, 27).—Aromatic acylguanidines are best prepared by boiling the aromatic acylcyanamides with the hydrochloride of an aromatic amine in alcoholic solution; thus benzoylcyanamide and aniline hydrochloride yield benzoylphenylguanidine, the *hydrochloride* of which has m. p. 159°. *Benzoyl-m-tolylguanidine*, $C_7H_8{\cdot}NH{\cdot}C(NHBz){:}NH$, crystallises in needles or leaflets, m. p. 71°; the *hydrochloride* has m. p. 170°. *Cinnamoylphenylguanidine*,

$$CHPh{:}CH{\cdot}CO{\cdot}NH{\cdot}C(NHPh){:}NH,$$

forms prismatic needles, m. p. 140°; *benzoyl-ψ-cumidylguanidine*, $C_{17}H_{19}ON_3$, occurs in prismatic needles, m. p. 140—141°.

On boiling acylcyanamides with *o*-phenylenediamine in alcoholic solution, an acylaminobenziminazole is produced. The arylcyanamides do not readily undergo this condensation. *Cinnamoyl-o-phenylene-guanidine* [*2-cinnamoyliminobenziminazole*],

$$C_6H_4{<}\begin{matrix}NH\\NH\end{matrix}{>}C{:}N{\cdot}CO{\cdot}CH{:}CHPh,$$

crystallises in needles, m. p. 262°. W. O. W.

Pechmann's Isomeric Hydrazidines. HENRY L. WHEELER and TREAT B. JOHNSON (*Ber.*, 1911, **44**, 151).—The authors have already shown (Abstr., 1904, i, 628) that the formulæ suggested by Busch and Ruppenthal (this vol., i, 86) for Pechmann's hydrazidines (Abstr., 1896, i, 31), namely, $NH_2{\cdot}NPh{\cdot}CPh{:}NPh$ and $NHPh{\cdot}NH{\cdot}CPh{:}NPh$, are correct. J. J. S.

Preparation of 4-*iso*Valerylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone and of 4-α-Bromo*iso*valerylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone. KNOLL & Co. (D.R.-P. 227013).—Compounds possessing valuable therapeutic properties are obtained by introducing *iso*valeryl or substituted *iso*valeryl residues into 4-amino-1-phenyl-2 : 3-dimethyl-5-pyrazolone.

4-iso*Valerylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone*, m. p. 203°, odourless and with a bitter taste, is prepared by heating 4-amino-1-phenyl-2 : 3-dimethyl-5-pyrazolone with *iso*valeric acid and phosphorus trichloride at 125° during half an hour, treating with sodium carbonate, and crystallising the dried product from benzene; its aqueous solutions give a blood-red coloration with ferric chloride.

4-α-*Bromoisovalerylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone* is obtained when α-bromo*iso*valeryl bromide is substituted for the *iso*valeric acid and phosphorus trichloride in the foregoing preparation; it forms glistening, colourless needles, m. p. 206° (decomp.), is odourless, but has a bitter taste, and forms crystalline *salts* with acids and a yellow coloration with ferric chloride. F. M. G. M.

Preparation of 4-Imino-5-oximino-2 : 6-diketopyrimidine and its 3-Alkyl Derivative. EMANUEL MERCK (D.R.-P. 227390).—The action of nitrous acid on a hot dilute acetic acid solution of cyano-

acetylmethylcarbamide, $NHMe{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}CN$, yields *oximinocyanoacetylmethylcarbamide*, $NHMe{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}C(:NOH){\cdot}CN$, colourless crystals, m. p. 218° (decomp.). When this substance is warmed with 30% sodium hydroxide (4 parts), an orange-yellow precipitate slowly separates, which on the addition of acetic acid is converted into the characteristic red crystals of 4-imino-5-oximino-2 : 6-diketo-3-methylpyrimidine, $NH<\begin{matrix}CO{\cdot}C(:NOH)\\CO\text{——}NMe\end{matrix}>C:NH$. Analogous results are obtained when cyanoacetylcarbamide is employed in the foregoing reaction; a yellow, crystalline *sodium* derivative separates on treatment with sodium nitrite, yielding on acidification *oximinocyanoacetylcarbamide*, glistening, colourless crystals, m. p. 220°, which are readily converted into the corresponding 4-imino-5-oximino-2 : 6-diketopyrimidine. The sodium hydroxide can in this reaction be replaced by sodamide, sodium ethoxide, or an alkylcarbamide. F. M. G. M.

Preparation of Anthrapyrimidines and Anthrapyrimidones. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 225982).—The reaction between aminoanthraquinones and acid amides has been previously described (Abstr., 1910, i, 445); the same result is now obtained with acylaminoanthraquinones and ammonia, 1-anthrapyrimidone (*loc. cit.*) having been prepared by heating aminoanthraquinoneurethane with ammonium hydroxide at 150°; likewise, 1 : 4-diaminoanthraquinonemonourethane yields 4-*amino*-1-*anthrapyrimidone*, brown crystals, and 2-*bromo*-4-*amino*-1-*μ-methylanthrapyrimidine*, a brown powder, is obtained from 2 : 4-dibromo-1-acetylaminoanthraquinone.

A tabulated description of the following compounds, with the colours of their solutions in various solvents, is given in the original: 1-*aminoanthraquinoneurethane*, greenish-yellow crystals; 1-*aminoanthraquinonecarbamide chloride*, orange crystals; 1 : 4-*diaminoanthraquinonemonourethane*, garnet-red crystals; 4-*chloro*-1-*aminoanthraquinoneurethane*, golden-yellow crystals; 2 : 4-*dibromo*-1-*acetylaminoanthraquinone*, brownish-yellow crystals; 4-*amino*-1-*anthrapyrimidone*, dark brown crystals. F. M. G. M.

4-Dibromo-1 : 2 : 3-triazol-5-one-1-acetamide. Theodor Curtius and Ernst Welde (*Ber.*, 1910, 43, 857—862).—The dibromo-derivative mentioned previously (Abstr., 1907, i, 450) is shown to be 4-*dibromo*-1 : 2 : 3-*triazole*-5-*one*-1-*acetamide*,

$$\begin{matrix}N{=}{=}N\\|\\CBr_2{\cdot}CO\end{matrix}>N{\cdot}CH_2{\cdot}CO{\cdot}NH_2.$$

Its formation from the ammonium salt of 5-hydroxy-1 : 2 : 3-triazole-1-acetamide is represented by means of the equation:

$$\begin{matrix}N{=}{=}{=}{=}N\\|\\CH:C(O{\cdot}NH_4)\end{matrix}>C{\cdot}CH_2{\cdot}CO{\cdot}NH_2 + 2Br_2 =$$

$$C_4H_4O_2N_4Br_2 + HBr + NH_4Br,$$

and its formation from the nitroso-derivative by the equation:

$$C_4H_8O_3N_5 + 2Br_2 = C_4H_4O_2N_4Br_2 + NOBr + NH_4Br,$$

the nitrosyl bromide formed immediately yielding nitrous and hydrobromic acids.

The dibromo-derivative crystallises from hot alcohol in colourless, glistening needles, m. p. 151° (decomp.), after turning brown at 120°. It changes colour when exposed to the air for several hours, and then has an odour of bromine. When boiled with dilute sulphuric acid, it is hydrolysed to nitrogen, ammonia, glycine, and dibromoglycollic acid, the last of which is further hydrolysed to hydrobromic and oxalic acids. The same decomposition occurs, only more slowly, when the bromo-derivative is boiled with water. J. J. S.

Derivatives of *iso*Uric Acid. Heinrich Biltz (*Ber.*, 1910, 43, 3553—3562).—It has been shown (Abstr., 1909, i, 740) that diethoxy-4 : 5-diphenyldihydroglyoxalone is converted on heating at the m. p. into 5-ethoxy-4 : 5-diphenyl*iso*glyoxalone. Diethoxy-1 : 3 : 7-trimethyluric acid might be expected to behave similarly, but it does not change at the m. p. However, on boiling it in glacial acetic acid solution, *5-ethoxy-trimethylisouric acid*, $\begin{matrix}NMe\cdot CO\cdot C(OEt)\\ |\\ CO\cdot NMe\cdot C\cdot N\cdot CO\end{matrix}>NMe$, is formed. This can be crystallised from cold alcohol without change, but on boiling with alcohol containing a little acid, the diethoxy-derivative is regenerated. On reduction with zinc and acetic acid, hydrogen is added at positions 4 and 9, that in 4 is immediately eliminated with the ethoxyl group in position 5, and trimethyluric acid is obtained.

5-Ethoxytrimethyl*iso*uric acid is completely analogous to 5-ethoxy-diphenyl*iso*glyoxalone, and the conclusion is drawn that the ethoxyl group in position 4 and the imino-hydrogen in position 9 are on opposite sides of the plane of the glyoxalone ring.

By the action of chlorine on trimethyluric acid in chloroform solution, a dichloride is first formed soluble in chloroform, chlorine being added in positions 4 and 5. This is unstable, hydrogen chloride being eliminated between positions 4 and 9, and a chlorine derivative of *iso*uric acid is obtained,

$$\begin{matrix}NMe\cdot CO\cdot CCl\cdot NMe\\ |\\ CO\cdot NMe\cdot CCl{-}NH\end{matrix}>CO \longrightarrow \begin{matrix}NMe\cdot CO\cdot CCl\cdot NMe\\ |\\ CO\cdot NMe\cdot C{=}N\end{matrix}>CO.$$

Alcohol converts this chloride into 5-ethoxy-1 : 3 : 7-trimethyl*iso*uric acid; water readily converts it into *apo*caffeine.

5-Ethoxy-1 : 3 : 7-trimethylisouric acid forms long, thin, colourless needles, m. p. 174—176°.

5-Methoxy-1 : 3 : 7-trimethylisouric acid crystallises in obliquely cut, six-sided, columnar forms, m. p. 205°.

5-Chloro-1 : 3 : 7-trimethylisouric acid separates in colourless, flat needles or prisms with oblique end faces and a rectangular cross section, m. p. 158° (decomp.). The corresponding 5-bromo-compound could not be obtained. E. F. A.

Hydroxyazo-compounds and Ketohydrazones. I.—III. Karl Auwers [and, in part, Hugo Dannehl and A. Boennecke] (*Annalen*, 1910, 378, 210—260. Compare Auwers, Abstr., 1908, i, 477).—The results of previous investigations indicate that when possible the phenylhydrazones of benzoquinones and naphthaquinones undergo

molecular rearrangement into azo-compounds, whereas with mixed azo-derivatives the reverse process takes place.

Phenanthraquinonephenylhydrazone (Zincke, Abstr., 1883, 1135; Werner, *Annalen*, 1902, 321, 304), when benzoylated in the presence of pyridine, yields a benzoyl derivative which is identical with the product obtained by condensing phenanthraquinone with *as*-benzoylphenylhydrazine in the presence of mineral acids. From the readiness with which it is hydrolysed and from the fact that when reduced with zinc dust and cold acetic acid the chief products are aniline and 9-benzoylamino-10-hydroxyphenanthrene (87% yield), the conclusion is drawn that the benzoyl compound is an *O*-derivative:

$$\begin{matrix} C_6H_4\cdot C\cdot N{:}NPh \\ \quad\quad\quad\quad\ \ O \\ C_6H_4\cdot C\cdot OBz \end{matrix} \longrightarrow \begin{matrix} C_6H_4\cdot C\cdot NHBz \\ \quad\quad\quad\quad\ \ O \\ C_6H_4\cdot C\cdot OH \end{matrix} + NH_2Ph.$$

In the condensation of phenanthraquinone with benzoylphenylhydrazine, a wandering of the benzoyl group from nitrogen to oxygen occurs, a wandering analogous to that observed in the condensation of β-naphthaquinone with benzoylphenylhydrazine. The same *O*-acetyl derivative is obtained by acetylating phenanthraquinonephenylhydrazone and by condensing phenanthraquinone with *as*-acetylphenylhydrazine. This acetyl derivative is so readily hydrolysed that it is difficult to purify. The general conclusion drawn is that phenanthraquinonephenylhydrazone is 9-benzeneazo-10-phenanthrol.

9-Benzeneazo-10-phenanthryl benzoate, $C_{27}H_{18}O_2N_2$, crystallises from glacial acetic acid in glistening, red plates, m. p. 193—194°. *9-Benzoylamino-10-phenanthrol*, $C_{21}H_{15}O_2N$, crystallises from glacial acetic acid in glistening, flat needles, m. p. 248—249°. *9-Benzeneazo-10-phenanthryl acetate*, $C_{22}H_{16}O_2N_2$, crystallises from light petroleum in brilliant red plates, m. p. 139—140°, and is hydrolysed when warmed with alcohol or acetic acid.

The question as to the constitution of Knorr's 4-benzeneazo-5-keto-1-phenyl-3-methylpyrazolone has been investigated (Knorr, Abstr., 1887, 678; 1888, 724; Japp and Klingemann, Trans., 1888, 53, 519; Wedekind, *Annalen*, 1897, 295, 330; Bülow, Abstr., 1899, i, 355; Eibner, Abstr., 1903, i, 871). The same benzoyl derivative is obtained by: (1) the action of benzoyl chloride on the sodium derivative suspended in dry ether; (2) the action of benzoyl chloride and sodium hydroxide solution on an aqueous acetone solution of the pyrazolone; (3) the condensation of ketophenylmethylpyrazolone with *as*-phenylbenzoylhydrazine hydrochloride in dilute alcohol. It is regarded as the *O*-benzoyl derivative, $N\lessdot\begin{matrix} CMe\cdot C\cdot N{:}NPh \\ \quad\quad\quad\ \ O \\ NPh\cdot C\cdot OBz \end{matrix}$, since when reduced with zinc dust and cold acetic acid it yields appreciable amounts of aniline, together with benzanilide and rubazonic acid.

$$R\lessdot\begin{matrix} C\cdot N{:}NPh \\ \quad\quad O \\ C\cdot OBr \end{matrix} \longrightarrow R\lessdot\begin{matrix} C\cdot NH_2 \\ \quad\quad O \\ C\cdot OH \end{matrix} + NHPhBz.$$

$$\longrightarrow R\lessdot\begin{matrix} C\cdot NHBz \\ \quad\quad O \\ C\cdot OH \end{matrix} + NH_2Ph.$$

It has not been found possible to isolate the *N*-benzoyl derivative of the aminohydroxyphenylmethylpyrazole.

Knorr's compound is thus a true azo-derivative, and as it dissolves readily in alkalis, it is represented by the enolic formula

$$N\lessdot\begin{matrix}CMe\cdot C\cdot N:NPh\\ \|\\ NPh\cdot C\cdot OH\end{matrix}$$

and is 4-benzeneazo-5-hydroxy-1-phenyl-3-methylpyrazole.

When the β-phenylhydrazone of αβ-diketobutyric acid is condensed with benzoylphenylhydrazine, water is eliminated, and Knorr's azo-compound and ethyl benzoate are obtained, instead of the expected *N*-benzoyl derivative, $N\lessdot\begin{matrix}CMe\cdot C:N\cdot NPhBz\\ |\\ NPh\cdot CO\end{matrix}$. The free hydroxy-pyrazole is also formed (1) when the benzoylated osazone of the diketobutyric acid is warmed with benzene and phosphoric oxide; (2) when the β-phenylhydrazone of ethyl αβ-diketobutyrate is condensed with *as*-benzoylphenylhydrazine hydrochloride in alcoholic solution, both with and without the addition of sodium acetate, and (3) when the dibenzoyl derivative of the osazone of the ethyl diketobutyrate is warmed with alcoholic potassium hydroxide.

The methyl derivative obtained by condensing ketophenylmethylpyrazolone with *as*-phenylmethylhydrazine must be the *N*-methyl ether, $N\lessdot\begin{matrix}CMe\cdot C:N\cdot NMePh\\ |\\ NPh\cdot C:O\end{matrix}$, as alkyl groups do not wander under these conditions. This constitution is confirmed by the fact that when reduced with zinc and acetic acid, methylaniline is obtained, but no trace of aniline. The same methyl ether, together with a small amount of the isomeric *O*-methyl ether, $N\lessdot\begin{matrix}CMe\cdot C\cdot N:NPh\\ \|\\ NPh\cdot C\cdot OMe\end{matrix}$, is formed when Knorr's azo-compound is methylated by means of methyl iodide or sulphate and alkali. When reduced, the *O*-methyl ether yields appreciable amounts of aniline.

The *N*-methyl ether is readily hydrolysed to the monomethyl derivative of ethyl diketobutyrate osazone, whereas the *O*-ether is not acted upon when boiled with alcoholic potassium hydroxide.

The *benzoyl* derivative of 4-benzeneazo-5-hydroxy-1-phenyl-3-methylpyrazole, $C_{23}H_{18}O_2N_4$, crystallises from alcohol in long, yellow, glistening needles, or from light petroleum in quadratic plates, m. p. 137°, which are readily hydrolysed when boiled with 50% acetic acid.

The *dibenzoyl* derivative of *4-amino-5-hydroxy-1-phenyl-3-methylpyrazole*, $N\lessdot\begin{matrix}CMe\cdot C\cdot NHBz\\ \|\\ NPh\cdot C\cdot OBz\end{matrix}$, prepared by benzoylating the corresponding amine, crystallises from dilute alcohol in colourless, glistening needles m. p. 196°, and on hydrolysis yields a colourless compound, m. p. 110—115°, probably the acid $NHPh\cdot N:CMe\cdot CH(NHBz)\cdot CO_2H$, which when heated, yields the *N-benzoyl* derivative, $N\lessdot\begin{matrix}CMe\cdot CH\cdot NHBz\\ |\\ NPh\cdot CO\end{matrix}$, m. p. 183°. Keto-1-phenyl-3-methylpyrazolone, prepared by Sachs and Barschall's method (Abstr., 1902, i, 504), has m. p. 121°. The monobenzoylosazone of αβ-diketobutyric acid,

$$NHPh\cdot N:CMe\cdot C(CO_2H):N\cdot NBzPh,$$

crystallises from light petroleum in slender, pale yellow needles, m. p.

0—111°, and dissolves in cold sodium hydroxide solution without dergoing hydrolysis. Ethyl $a\beta$-diketobutyrate and benzoylphenyl-drazine yield the *dibenzoylated osazone*, $C_{32}H_{28}O_4N_4$, even in the esence of an excess of ester. It crystallises from dilute methyl cohol in long, colourless prisms, m. p. 190°. Ethyl $a\beta$-diketobutyrate id phenylmethylhydrazine yield the *dimethylosazone*,

$$NMePh\cdot N{:}CMe\cdot C(CO_2Et){:}N\cdot NMePh,$$

hich crystallises from alcohol in pale yellow, glistening prisms, m. p. 3—104°. The *phenylmethylhydrazone* of 4-keto-1-phenyl-3-methyl-pyrazolone, $C_{17}H_{19}ON_4$, crystallises from dilute alcohol in glistening, ange-yellow, felted needles, m. p. 144°, and is insoluble in alkalis; ie isomeric O-*methyl ether* forms compact, yellow prisms, m. p. 78°.

It has not been found possible to acetylate or benzoylate Graebe and feller's acenaphthenequinonephenylhydrazone (Abstr., 1893, i, 657), it the *benzoyl* derivative, $C_{25}H_{16}O_2N_2$, can be prepared by con-ensing the quinone with benzoylphenylhydrazine hydrochloride and cohol. It crystallises in glistening, orange-red needles, m. p. 170°, and readily hydrolysed by cold alcoholic sodium hydroxide. When duced with zinc and acetic acid, it yields no trace of aniline, and is ierefore a *N*-benzoyl derivative, and the phenylhydrazone probably is the hydrazone and not the azo-structure.

Acenaphthenequinonephenylmethylhydrazone, $C_{19}H_{14}ON_2$, crystallises om acetone in dark red needles, m. p. 114°, and, when reduced, elds methylaniline and no trace of aniline.

Camphorquinonephenylhydrazone cannot be directly acylated, but ie *benzoyl* derivative, $C_{23}H_{24}O_2N_2$, can be obtained, by condensing ie quinone with benzoylphenylhydrazine, in the form of colourless, lted needles, m. p. 153°. This is also a *N*-benzoyl derivative, and ie parent substance a hydrazone, which exists in one form only ompare Lapworth and Hann, Trans., 1902, 81, 1514).

The two *N*-benzoyl derivatives, unlike most other *N*-benzoylated mpounds, are readily hydrolysed. The following new *N*-benzoyl erivatives, prepared by condensing the ketones with benzoylphenyl-ydrazine, are not readily hydrolysed by alkalis: *Ethyl acetoacetate nzoylphenylhydrazone*, $C_{19}H_{20}O_3N_2$, forms compact, colourless, adratic crystals, m. p. 144—145°, and with alcoholic potash elds the *benzoylphenylhydrazone* of acetoacetic acid, $C_{17}H_{16}O_3N_2$, in e form of small, colourless prisms, m. p. 203°.

Diacetyldibenzoylosazone, $C_{30}H_{26}O_2N_4$, crystallises from boiling glacial etic acid in slender needles, m. p. 249°, and is formed even at −15° the presence of an excess of the ketone. *Benzil-benzoylphenyl-drazone*, $C_{27}H_{20}O_2N_2$, crystallises from light petroleum in slender, ismatic needles, m. p. 176°.

Baeyer and Claisen's phenylazoacetylacetone (Abstr., 1888, 828) is st prepared by the gradual addition of a solution of phenyl-zonium chloride exactly neutralised with sodium carbonate to a ld solution of acetylacetone (1 mol.) in sodium carbonate (0·5 mol.). ie benzoyl derivative (Pechmann, Abstr., 1893, i, 84) is most dily prepared by the Schotten-Baumann method; it has m. p. 0—161°, is readily hydrolysed by alkalis, and is sometimes accom-nied by an *isomeride*, m. p. 134°. When reduced, the benzoyl

derivative yields benzanilide, but no trace of aniline. The compound is thus a *N*-benzoyl derivative, and the parent substance a γ-phenyl hydrazone of βγδ-triketopentane and not an azo-derivative.

Benzoylacetylacetone, in the form of its sodium derivative, reacts with a neutralised solution of phenyldiazonium chloride, yielding *O-benzeneazodiacetylbenzoylmethane*, NPh:N·O·CMe:CBzAc, which crystallises from methyl alcohol in golden-yellow, prismatic needles, m. p. 77—78°. The compound is not affected when boiled with alcohol; with cold alkalis, or with an ethereal solution of hydrogen chloride, it yields the phenylhydrazone of phenyl methyl triketone, and when boiled with glacial acetic acid yields benzoylacetone. The reaction with hydrogen chloride is similar to that described by Dimroth and Hartmann as characteristic of *O*-azo-compounds (Abstr., 1909, i, 66). The azo-compound (m. p. 77—78°) reacts with an alcoholic solution of β-naphthol, yielding benzeneazo-β-naphthol and benzoylacetylacetone. When reduced with zinc dust and acetic acid, the azo-compound yields appreciable amounts of aniline. The isomeric *acetylphenylhydrazone* of phenyl methyl triketone,

CAcBz:N·NAcPh,

is formed when the *O*-azo-compound is boiled for four hours with toluene; it separates from alcohol in colourless crystals, m. p. 158°, and when reduced yields acetanilide, but no trace of aniline. The compound is isomeric with the benzoyl derivative of phenylazoacetylacetone, m. p. 160°.

These results agree with Pechmann's view that the compounds derived from diazo-compounds and aliphatic ketones with the reactive ·CO·CH_2· group are not azo-compounds, but hydrazones.

Generalisations based on the constitution of *N*-benzoyl derivatives and the readiness with which they are hydrolysed cannot be drawn.

J. J. S.

Method for Determining the Individuality or Plurality of Diastases in a Liquid. Pierre Achalme and Bresson (*Compt. rend.*, 1910, 151, 1369—1372).—In order to ascertain whether a particular liquid contains one or more enzymes, the authors suggest that it should be allowed to act, under identical conditions, on solutions of two different substances capable of being hydrolysed by it, and on a solution containing a mixture of the same two substances. If two diastases are present, the action on the mixture should be the sum of the action on the two substances taken individually, whilst if only one enzyme is present, the action on the mixture should not exceed that on either substance alone. The results of illustrative experiments are given in tabular form. It is found that the time taken to effect hydrolysis in the three solutions is the same if two diastases are present, but that when only one enzyme is acting, a longer period is required to hydrolyse the mixture.

W. O. W.

Chlorophyll. XI. Chlorophyllase. Richard Willstätter and Arthur Stoll (*Annalen*, 1910, 378, 18—72).—See this vol., i, 141.

Organic Chemistry.

Synthesis of *as*-Heptachloropropane from Tetrachloroethylene and Chloroform with the Co-operation of Aluminium Chloride. Jacob Böeseken and H. J. Prins (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 13, 685—687).—It has previously been shown (Abstr., 1910, i, 152) that when dichloroacetyl chloride is decomposed by aluminium chloride, one of the products is a crystalline substance, m. p. 32°, to which the composition C_3Cl_{10} was assigned. A larger quantity of this substance has now been prepared, and it is found to be identical with the *as* heptachloropropane obtained by Fritsch from pentachloroacetone and phosphorus pentachloride (Abstr., 1898, i, 63). The heptachloropropane may also be prepared by the direct addition of chloroform to tetrachloroethylene under the influence of aluminium chloride.

This synthesis gives another proof that the theory of the formation of intermediate products as an explanation of Friedel and Crafts' reaction must be abandoned, as there are no indications of the formation of such products. It may be assumed that aluminium chloride renders the chloroform active, so that the molecular parts $CHCl_2$ and Cl attach themselves to the double linking of the ethylene perchloride, also rendered active.

It is also shown that pentachloroethane yields *as*-heptachloropropane with chloroform and aluminium chloride. N. C.

Preparation of Bromides from Primary and Secondary Saturated Alcohols. Felix Taboury (*Bull. Soc. chim.*, 1911, [iv], 9, 124—125).—Fournier (Abstr., 1906, i, 787) has shown that hydrogen bromide reacts with primary and secondary saturated alcohols at the ordinary pressure, giving good yields of alkyl bromides. The author states that it is unnecessary to prepare the hydrogen bromide separately, and gives details for carrying out the reaction in one large flask. Yields varying from 75 to 85% of methyl, ethyl, propyl, and *iso*propyl bromides were obtained in this way. In the case of *iso*butyl bromide the yield fell to 50%, owing to a secondary action of the bromine on the bromide produced. It was found in this case that on raising the temperature at the end of the experiment, a liquid was obtained, b. p. 149—150°; this is dibromo*iso*butane, $CH_2Br\cdot CMe_2Br$. N. C.

Acetylenic Pinacone [$\beta\epsilon$-Dimethyl-Δ^{γ}-hexinene-$\beta\epsilon$-diol]. Georges Dupont (*Compt. rend.*, 1911, 152, 197—199). —$\beta\epsilon$-Dimethyl-Δ^{γ}-hexinene-$\beta\epsilon$-diol, $OH\cdot CMe_2\cdot C{:}C\cdot CMe_2\cdot OH$ (Jotsitch, *J. Russ. Phys. Chem. Soc.*, 1904, 36, 1545) is a colourless substance, m. p. 95°, which, unlike corresponding saturated compounds, does not form a hydrate. It resembles these subtances, however, in its behaviour towards the halogen acids, but approaches more closely to $\beta\delta$-dimethylpentane-

$\beta\delta$-diol (Franke, Abstr., 1905, i, 111; 1907, i, 816) in its reactions with dehydrating agents.

The corresponding *dibromide*, $CMe_2Br\cdot C{:}C\cdot CMe_2Br$, m. p. 39°, b. p. 219°, is an exceedingly stable substance. In its formation by the action of hydrogen bromide, an unstable intermediate compound was noticed, m. p. about 50°. The corresponding *dichloride* has m. p. 29°, b. p. 62—63°/15 mm.

By the action of dilute sulphuric acid on the diol, the two following substances are obtained in proportions varying with the concentration and duration of heating. (1) *β-Methyl-ε-methylene-Δγ-hexinene-βε-diol*, $CH_2{:}CMe\cdot C{:}C\cdot CMe_2\cdot OH$, a pale yellow liquid with an agreeable odour, m. p. −2°, b. p. 159—160°, D^{15} 0·8772, n_D 1·4687. When treated with hydrogen in presence of spongy platinum it yields dimethyl-*iso*amylcarbinol (Konowaloff, Abstr., 1902, i, 336). (2) *βε-Dimethylene-Δγ-hexinene*, $CH_2{:}CMe\cdot C{:}C\cdot CMe{:}CH_2$, is a colourless, mobile liquid, b. p. 123—124°, D^{15} 0·7898, n_D 1·4859, which rapidly becomes resinous on exposure to air. It is best prepared by the action of potassium hydroxide on the foregoing dibromide. On reduction it yields *βε*-dimethylhexane. W. O. W.

Existence of Chlorosulphinic Esters. Arthur Stähler and Erik Schirm (*Ber.*, 1911, **44**, 319—323).—Well-cooled ethyl alcohol is treated slowly with thionyl chloride, and the mixture is distilled under 19 mm. pressure after being kept overnight. The resulting ethyl chlorosulphinate, $Cl\cdot SO_2Et$, b. p. 29°/13 mm., is a faintly yellow liquid, which decomposes at its b. p., 122°, under ordinary pressure into sulphur dioxide and ethyl chloride, as found by previous investigators. The methyl ester, b. p. 19°/13 mm. or 102°/755 mm. (decomp.), is obtained, and behaves in a similar manner. Neither of the esters, however, can be separated completely from the excess of the thionyl chloride on account of proximity of b. p. The *propyl* ester, however, has been obtained in a pure state as a colourless liquid, b. p. 78°/75 mm. The *isobutyl* ester has b. p. 48·5°/9 mm.

The chlorosulphinic esters are very unstable substances, which are vigorously decomposed by water into sulphur dioxide, hydrogen chloride, and an alcohol. C. S.

Delepine's Phosphorescent Esters. Jaime Ferrer Hernández and Angel del Campo y Cerdan (*Anal. Fis. Quim.*, 1911, **9**, 17—26. Compare Delepine, Abstr., 1910, i, 295, 545).—The authors have repeated Delepine's observations on the phosphorescence of dimethyl dithiocarbonate, $OMe\cdot CS\cdot SMe$, and find that ionisation of the air is produced during the phenomenon, whilst the compound appears to possess feeble radioactivity. The potassium methyl salt, $OMe\cdot CS\cdot SK$ yields methyl tetrathionate when oxidised by potassium permanganate or sodium perborate in dilute acid solution. G. D. L.

Separation of the Liquid Fatty Acids (Unsaturated) from the Solid Fatty Acids (Saturated) in Natural Mixtures of Fatty Acids, and the Ammonium Salts of Some Fatty Acids. II. Pietro Falciola (*Gazzetta*, 1910, **40**, ii, 425—435. Compare this vol., i, 5).—When applied to mixtures of natural origin

the method previously described does not effect a rigorously quantitative separation, but nevertheless it may be employed with more or less success, and yields more satisfactory results in the case of mixtures containing a preponderance of the solid acids. The ammonium salts of the solid fatty acids (such as the palmitate and stearate) are more soluble in ammoniacal alcohol containing ammonium salts of liquid fatty acids (for example, the oleate) than in that solvent alone. Moreover, the solid fatty acids separated by the method always contain appreciable quantities of the liquid fatty acids.

Ammonium linoleate, $C_{17}H_{31}\cdot CO_2\cdot NH_4$, is prepared by passing dry ammonia into a cold ethereal salution of the acid in an atmosphere of hydrogen. In presence of ammonia and lime, the pasty mass obtained becomes solid. It begins to melt at 57—58°, and is completely melted at 75°, forming a red liquid. *Ammonium erucate*, $C_{22}H_{41}O_2\cdot NH_4$, is similarly prepared, and has m. p. 70—77°. *Ammonium laurate*, $C_{11}H_{23}\cdot CO_2\cdot NH_4$, is a white substance, m. p. about 75°. *Ammonium myristate*, $C_{13}H_{27}\cdot CO_2\cdot NH_4$, has m. p. about 75—90°. *Ammonium hexoate*, $C_8H_{15}O_2\cdot NH_4$, has m. p. 70—85°. Ammonium hexoate may be prepared in the same way. *Ammonium crotonate*, $C_3H_4\cdot CO_2\cdot NH_4$, forms colourless crystals, m. p. 105—115°. *Ammonium butyrate*, $C_3H_7\cdot CO_2\cdot NH_4$, has m. p. 70—85°. R. V. S.

Linolenic Acid and Linseed Oil. Adolf Rollett (*Zeitsch. physiol. Chem.*, 1911, 70, 404—407).—Polemical (compare Erdmann and Bedford, Abstr., 1910, i, 810; Rollet, Abstr., 1909, i, 760). Pure linolenic acid has the iodine value 273·7. E. F. A.

Action of the Chlorides of α-Alkyloxy-acids on Organometallic Derivatives of Zinc. Edmond E. Blaise and L. Picard (*Compt. rend.*, 1911, 152, 268—269).—The chlorides of α-alkyloxy-acids are acted on abnormally by organozinc iodides, giving rise under some conditions to an ether, in addition to the usual alkyloxy-ketone. This arises from the elimination of carbon monoxide from the acid chloride, probably through catalytic influence of the zinc compound. The action is represented as: $R\cdot O\cdot CH_2\cdot COCl = R\cdot O\cdot CH_2Cl + CO$; $R\cdot O\cdot CH_2Cl + ZnR'I = ZnClI + R\cdot O\cdot CH_2R'$. The yield of ether increases and that of ketone diminishes as the temperature of reaction rises. The proportion of ether increases also with the molecular weight of the zinc salt; thus, from zinc *n*-heptyl iodide only ethyl octyl ether was obtained. When R or R' are cyclic, only the ketone is formed; thus ethoxyacetyl chloride and zinc *p*-tolyl bromide gave *p-tolyl ethoxymethyl ketone*, $OEt\cdot CH_2\cdot CO\cdot C_7H_7$, b. p. 135°/9·5 mm.; the *oxime* has m. p. 57°, and the *p-nitrophenylhydrazone*, m. p. 80°. The yield of ketone increases also with the weight of R. *iso*Butoxyacetyl chloride and zinc ethyl iodide gave *n*-propyl *iso*butyl ether (10%) and *ethyl isobutoxymethyl ketone* (50%), b. p. 68—69°/13 mm.; *oxime*, b. p. 116—117°/14 mm.; *semicarbazone*, m. p. 72°. Phenoxyacetyl chloride gave only *phenoxymethyl ethyl ketone*, b. p. 129°/14 mm.; *semicarbazone*, m. p. 102°; *p-nitrophenylhydrazone*, prisms, m. p. 153°.

W. O. W.

The Preparation of β-Alkyloxy-compounds. M. H. Palkin and Sulo Kilpi (*Chem. Zentr.*, 1910, ii, 1453; from *Ann. Finn. Akad. Wiss.*, *A* 2, No. 3).—The preparation of the esters of hydracrylic acid by the action of sodium alkyloxides on ethyl β-chloropropionate gave unsatisfactory results; the action was better in the case of the β-iodopropionate. *Methyl β-methoxypropionate*, $OMe\cdot CH_2\cdot CH_2\cdot CO_2Me$, is a colourless liquid, b. p. 143·4—143·6°/750 mm., D^{15}_{15} 1·0148. *Ethyl β-ethoxypropionate* has b. p. 49·5—49·8°/7 mm., D^{15}_{15} 0·9536. *Propyl β-propoxypropionate* is a colourless, agreeably smelling liquid, b. p. 74·5—75·5°/7 mm., D^{15}_{15} 0·9386 N. C.

A Green, Crystalline Manganitartrate. André Job and P. Goissedet (*Compt. rend.*, 1911, 152, 265—268. Compare Abstr. 1907, ii, 553; Durrant, Trans., 1905, 87, 1781).—Eighteen grams of manganous sulphate dissolved in water (20 c.c.) are added to a solution of sodium tartrate (450 grams) in a litre of water. The solution is shaken in an atmosphere of oxygen, and 100 grams of sodium hydroxide in 250 c.c. of water added slowly. The red liquid gradually deposits green crystals of *sodium manganitartrate*,

$$\begin{matrix} CO_2Na\cdot CH\cdot O \\ | \\ CO_2Na\cdot CH\cdot O \end{matrix}\!\!>\!Mn\cdot O\cdot CH(CO_2Na)\cdot CH(ONa)\cdot CO_2Na,11H_2O.$$

This salt dissolves in water, forming an alkaline solution, which deposits manganic hydroxide and probably, through hydrolysis having occurred, contains the salt, $\begin{matrix} CO_2Na\cdot CH\cdot O \\ | \\ CO_2Na\cdot CH\cdot O \end{matrix}\!\!>\!Mn\cdot OH$. On the addition of sodium tartrate the liquid becomes green and remains stable. The green solutions are unable to afford green crystals although these appear on the addition of an alkali carbonate, when the liquid becomes red. An explanation of this fact is suggested. W. O. W.

Basic Citrates and Tartrates of Barium. Antonio Quartaroli (*Chem. Zentr.*, 1910, ii, 1131—1132; from *Staz. sperim. agrar. ital.* 1910, 43, 396—408).—The author states than when excess of barium hydroxide is added to a solution of citric acid at a temperature of at least 18°, a tetrabasic citrate is formed; at lower temperatures (+5—10°) a less basic citrate is formed, which is more soluble. The citrate formed above 18° dissolves to the extent of 10—13% in water. With tartaric acid, in the same way, a tribasic tartrate is obtained; the same modification is formed at 18° and at 5—10°, but at 100° a crystalline form is obtained. N. C.

Preparation of Formaldehyde from Methyl Alcohol by the Contact Process. Max Le Blanc and E. Plaschke (*Zeitsch. Elektrochem.*, 1911, 17, 45—57).—A constant, measured current of air is passed through methyl alcohol, kept at a constant temperature. The mixture of air and alcohol vapour, then passes over a spiral of silver, silver-plated copper, or copper gauze, and the products (consisting of formaldehyde, unchanged methyl alcohol, carbon monoxide and dioxide, hydrogen and nitrogen) are collected and analysed.

The maximum yield of formaldehyde is always obtained at about the same temperature. Measured near the end of the silver gauze spiral at which the gases entered it, the best temperature is 450°, but this is not the maximum temperature of the spiral, which often reaches a bright red heat in the middle. When the temperature of the contact is kept constant and the ratio of air to alcohol in the mixture is gradually increased, the yield of aldehyde increases to a maximum and then diminishes again. The maximum yield is obtained with about 0·46 gram of oxygen to 1 gram of alcohol. The loss of alcohol (the part not accounted for by aldehyde or unchanged alcohol in the products) increases rapidly and continuously as the oxygen is increased. The length of the contact layer also affects the results; in the 30 mm. tube used by the authors, the most favourable length was 70 mm., which gave the highest yield of formaldehyde observed, namely, 58% of the theoretical quantity.

The results with copper were very similar to those obtained with silver, the best length of layer being 80—90 mm., and the best mixture containing 0·39 gram of oxygen per gram of methyl alcohol.

A consideration of the composition of the gaseous products (which always contain more hydrogen than the sum of the carbon monoxide and dioxide) leads to the conclusion that the formation of formaldehyde is due, not to oxidation of methyl alcohol, but rather to its decomposition, thus: $CH_3{\cdot}OH = CH_2O + H_2$. The main source of loss is the decomposition of formaldehyde by heat: $CH_2O = CO + H_2$. To test this, methyl alcohol vapour was passed over freshly reduced copper at 300°. The yield of formaldehyde is fairly good at first, but falls off rapidly. (In six experiments with the same spiral, it fell from 28% in the first to 4% in the sixth.) The activity of the copper is restored by oxidising it and reducing it again. It appears, therefore, that the function of the air in the usual contact process is to keep the copper constantly in its most active form by continually oxidising it, the reduction being brought about by the hydrogen and carbon monoxide present. T. E.

Electrosyntheses. VI. Sima M. Losanitsch (*Ber.*, 1911, **44**, 2—315. Compare Abstr., 1910, i, 542).—It has been shown previously (Abstr., 1897, i, 179) that under the action of the silent discharge a mixture of carbon monoxide and hydrogen gives formaldehyde, which immediately condenses to yellow aldehydic products. Further investigation shows that these products consist of a liquid portion, soluble in water, alcohol and ether, and a solid portion, which is only soluble in water. The liquid portion is viscous, has the odour of paraldehyde, and contains formic acid. The yellow, solid portion has a composition corresponding with $C_{12}H_{18}O_{11}$. It is probably the first anhydride of $C_6H_{12}O_6$, since cryoscopic experiments show that the freshly made aqueous solution contains molecules corresponding with $C_{12}H_{18}O_{11}$, and these, on keeping, split up into $C_6H_{12}O_6$ molecules. Evaporation of the aqueous solution on the water-bath leaves a dark residue with the composition $C_6H_8O_5$; if the evaporation is carried out in a vacuum, the yellow compound, $C_{12}H_{18}O_{11}$, is left.

The aqueous solution of the yellow solid readily gives glyoxal

phenylosazone with phenylhydrazine, and glyoxime with hydroxylamine, from which it is probable that the yellow solid is a readily decomposable condensation product of glyoxal.

The formaldehyde produced from the carbon monoxide and hydrogen by the silent discharge probably condenses to the two following aldehydes: $2CH_2O = OH{\cdot}CH_2{\cdot}CHO$ and $2CH_2O = CHO{\cdot}CHO + H_2$, and these then form the compound $CHO{\cdot}CHO,2OH{\cdot}CH_2{\cdot}CHO$, which is the yellow solid.

The condensation product obtained from carbon monoxide and methane (Abstr., 1908, i, 866) also contains a part soluble and a part insoluble in water. The former is identical with the above yellow solid, $C_{12}H_{18}O_{11}$.

A mixture of carbon dioxide and hydrogen behaves similarly to a mixture of carbon monoxide and hydrogen towards the silent discharge, since the carbon dioxide is first reduced to the monoxide.

T. S. P.

α-Bromocrotonaldehyde. Paul L. Viguier (*Compt. rend.*, 1911, **152**, 269—271. Compare Abstr., 1909, i, 691; 1910, i, 461).—α-Bromocrotonaldehyde forms an *oxime*, m. p. 110—111°, which becomes pasty on keeping. The *semicarbazone* has m. p. 228—230°. 5-Methylpyrazole is produced when the aldehyde is added to an alcoholic solution of hydrazine hydrate. The *phenylhydrazone*, lamellæ, m. p. 124—125°, is unstable; when treated with alcoholic potassium hydroxide, it forms 1-phenyl-5-methylpyrazole; on heating with excess of phenylhydrazine, it furnishes a *compound*, $C_{16}H_{15}N_4$, m. p. 117—119°.

When α-bromocrotonaldehyde or its acetal is allowed to act on urethane in aqueous solution in presence of a little hydrochloric acid, a *compound*, $C_{13}H_{21}O_6N_2Br$, is obtained. This crystallises in colourless, slender needles, m. p. 124—125°, and is useful for characterising the aldehyde.

W. O. W.

Photochemical Synthesis of Carbohydrates from Carbon Dioxide and Hydrogen in the Absence of Chlorophyll. Julius Stoklasa and Wenzel Zdobnický (*Biochem. Zeitsch.*, 1911, 30, 433—456; *Monatsh.*, 1911, **32**, 53—75).—A figure is given of the apparatus employed for carrying out experiments in the presence of ultra-violet light, the chief feature of which is the form of the basin in which the reactions were investigated, which was suspended from a mercury-quartz lamp which served as the source of light. It was found that water does not act on carbon dioxide in ultra-violet light in the absence of potassium hydroxide, neither formaldehyde nor carbohydrate being formed in this case. If potassium hydroxide is added, however, formaldehyde, but no carbohydrate, is formed. The hydrogen must be in the nascent state for the reaction to take place, and ultra-violet light must be present. In the absence of the latter, formic acid is formed. A sugar is also formed when nascent hydrogen reacts with carbon dioxide in the presence of ultra-violet rays. The nature of the carbohydrate has not yet been definitely established. The osazone melts at 196—200°, and is not, therefore, either formose, β-formose, or β-acrose.

S. B. S.

Nomenclature of the Sugars. EMIL VOTOČEK (*Ber.*, 1911, **44**, 360—361).—The prefix *epi* is used to denote the new carbohydrate formed by the interchange of the H and OH groups on the α-carbon atom: thus mannose becomes *epi*glucose, ribose becomes *epi*arabinose, talose becomes *epi*galactose, etc. The isomeric pair are spoken of as *epimerides*, and the change as *epimerism*. The nomenclature is extended to the alcohols and acids of the carbohydrates. E. F. A.

***epi*Rhodeose.** EMIL VOTOČEK and CYRILL KRAUZ (*Ber.*, 1911, **44**, 362—365. See preceding abstract).—Rhodeonic acid, prepared by oxidation of rhodeose with bromine, is partly converted on heating with pyridine at 150—160° into epi*rhodeonic acid*. The *barium* salt forms colourless, matted crystals, which are optically inactive. The crystalline *lactone* is reduced by sodium amalgam in the usual manner to epi*rhodeose*; this is a syrup, yielding the same phenylosazone as rhodeose, but the *methylphenylhydrazone* has m. p. 175°. On oxidation with nitric acid, the trihydroxyglutaric acid obtained has m. p. 184—185°, $[\alpha]_D$ +12°, falling to +2·5° on boiling, and differs slightly from the inactive lactone described by Fischer and Piloty (m. p. 179—171°; compare Abstr., 1892, 440). It is pointed out that ribohydroxyglutaric acid, although itself completely symmetric, forms a lactone, which is not symmetric. Fischer's lactone is an equimolecular mixture of *d*- and *l*-lactones, but that from *epi*rhodeose is possibly completely derived from *d*-lactone or from a mixture of *d*- and *l*-lactones in unequal proportions. E. F. A.

Solubility of Lime in Aqueous Solutions of Sucrose and of Glycerol. FRANK K. CAMERON and HARRISON E. PATTEN (*J. Physical Chem.*, 1911, **15**, 67—72).—When lime in excess is added to sucrose solution, a soluble compound of lime and sugar is formed, but some of the sucrose passes into the solid phase. The relation between the amount of lime dissolved and the amount of sucrose in solution is not a linear one, since the liquid is in equilibrium with a series of solid solutions of the lime-sucrose compound in lime. The solid phase, consisting of fine globular granules, was separated by a centrifuge, and contained upwards of 10·8% of sucrose.

Solutions containing more than 20% of sucrose could not be investigated owing to their high viscosity. The 20% solution dissolves about 6% of lime at 25°.

The presence of glycerol increases the solubility of lime to 1·31% in a 55% solution of glycerol. The ratio of lime to glycerol is a strictly linear one, and no glycerol passes into the solid phase. R. J. C.

Cellobiose and the Acetolysis of Cellulose. WILHELM SCHLIEMANN (*Annalen*, 1911, **378**, 366—381).—The treatment of cellulose (filter-paper or cotton wool) with a mixture of acetic anhydride and concentrated sulphuric acid at low temperatures yields products quite different from those obtained at higher temperatures, because the acetolysis (that is, the acetylation and hydrolysis of the cellulose molecule) is less quickened by the sulphoacetic acid produced in the acetylating mixture at high temperatures (Stillich,

Abstr., 1905, i, 318; 1906, i, 552, 626) than by the acetylsulphuric acid formed at low temperatures.

The product obtained by acetylating cellulose by Skraup and König's method (Abstr., 1902, i, 135) or by Maquenne and Goodwin's process (Abstr., 1904, i, 799), after hydrolysis by alcoholic potassium hydroxide, yields cellobiose, which, after being completely dried at 100°, has the formula $C_{12}H_{22}O_{11}$, and $[\alpha]_D^{20}$ 34·6° in 2—17% aqueous solutions. It can be estimated by Fehling's solution by Wein's method, and forms a *phenylosazone*, m. p. 208—210°, $[\alpha]_D$ −17·5° in alcoholic solution.

By treatment with acetic anhydride and sulphuric acid (or a little zinc chloride) it yields the same octa-acetylcellobiose, m. p. 221·5—222°, $[\alpha]_D^{20}$ 41·5° in chloroform, as is produced by the action of this acetylating mixture on cellulose (Maquenne and Goodwin, *loc. cit.*). The isomeric octa-acetylcellobiose, m. p. 191·5—192°, obtained by boiling cellobiose with acetic anhydride and sodium acetate, has $[\alpha]_D^{20}$ −7·8° in chloroform and −24·9° in benzene. Both octa-acetylcellobioses can be converted into the acetochloro-compound, m. p. 186—187° (Geinsperger, Abstr., 1906, i, 57; Hardt-Stremayr, Abstr., 1907, i, 389), from which, according to the author, silver acetate produces the octa-acetylcellobiose, m. p. 191°, $[\alpha]_D^{20}$ −7·5° in chloroform, whilst Geinsperger obtained an acetate, $[\alpha]_D$ −30·6° in chloroform, and Hardt-Stremayr an acetate, $[\alpha]_D$ 30·51°; the discrepancy is inexplicable.

In view of Jungius' experiments on the equilibrium of the penta-acetyldextroses (Abstr., 1905, i, 573), cellobiose and its two octa-acetyl derivatives have been treated with acetic anhydride and sulphuric acid, acetic anhydride and zinc chloride, and acetic anhydride and sodium acetate. The last-mentioned reagent does not change either of the octa-acetylcellobioses once it has been formed; with the other two reagents, mixtures of the two acetates are obtained, containing respectively 84% and 77% of the octa-acetyl compound, which has $[\alpha]_D^{20}$ 41·5° in chloroform. The two acetates in the mixture can be separated by cold benzene, in which the acetate, m. p. 191°, $[\alpha]_D^{20}$ −7·7° in chloroform, is the more soluble. Evidence is stated which indicates that the octa-acetylcellobiose, m. p. 191°, belongs to the β-series.

The amorphous by-products, obtained in addition to octa-acetylcellobiose by the acetolysis of cellulose, have been examined in regard to the content of acetic acid liberated by hydrolysis; the author is of opinion that the products containing 66·3—67·3% of acetic acid are the immediate precursors of the octa-acetylcellobiose. C. S.

Action of Water and of Alkali on Cotton Wool Cellulose. Carl G. Schwalbe and Michael Robinoff (*Zeitsch. angew. Chem.*, 1911, **24**, 256—258. Compare Tauss Dingler's *Polyt. Journ.*, 1880, **273**, 276; 1890, **276**, 411).—It is shown that the formation of hydrocelluloses, that is, compounds with strongly reducing properties, under the influence of water occurs only when the cellulose is partly altered; for example, filter-paper or strongly-bleached cellulose. With pure cellulose the formation of hydrocellulose is extremely small, even

under a pressure of 20 atmospheres. When a temperature of 150° is reached, marked decomposition of the cellulose occurs.

The action of dilute sodium hydroxide solutions on cellulose has been studied; the maximum effect at the ordinary temperature is obtained with a 4% alkali solution, as shown by the fact that the product after such treatment gives the highest copper values (corrected). At temperatures of 100° and above, the solubility increases, but diminishes as the concentration of the alkali is increased; at 150° the solubility is appreciable. The "gum value" has been obtained for a number of samples; by gum value is understood the weight of amorphous precipitate obtained by neutralising the alkaline extract. Pure cellulose has a "gum value" of practically nil, whereas impure forms have higher values. At 150°, however, the differences are small, and here it is also noticeable that the 4% alkali has the maximum effect. In treatment of cellulose, temperatures above 50°, and an alkali concentration of 4% are to be avoided. The acid used after bleaching should not be stronger than 0·1%; with still more dilute acid, a purer white is obtained, but the amount of oxycellulose is increased. J. J. S.

Action of Hydracids on Starch. II. William Oechsner de Coninck (*Bull. Acad. roy. Belg.*, 1910, 848—849. Compare Abstr., 1910, i, 655).—Starch (1·7 grams), water (50 grams), and hydrochloric acid (2 c.c.) after being left for seven minutes at 18·5° and then heated for four minutes gave a reddish-orange precipitate with Fehling's solution. Hydrobromic acid (1·5 c.c.) behaved similarly; hydriodic acid (1 c.c.) produced only a slight, although distinct, precipitate. After four hours at 17°, each acid had acted on starch sufficiently to cause slight reduction of Fehling's solution. E. F. A.

Dextrin. William Oechsner de Coninck and A. Reynaud (*Bull. Acad. roy. Belg.*, 1910, 846—847).—A mixture of 0·8 gram of dextrin, 40 grams of water, and twenty drops of concentrated hydrochloric acid gave a yellow precipitate with Fehling's solution (Cu_2O,H_2O) after twenty-four hours at 22°. With hydrobromic acid (twelve drops) the reduction (Cu_2O) was marked in five hours; with five drops of hydriodic acid, cuprous oxide (Cu_2O) was precipitated after five minutes' or five hours' action. With five drops of hydrochloric acid the precipitate with Fehling's solution was cuprous oxide; with ten drops, it consisted of a mixture of cuprous oxide and its hydrate, and with fifteen drops, it was entirely the hydrated oxide, Cu_2O,H_2O.

E. F. A.

Formation of Crystalline Polysaccharides (Dextrins) from Starch Paste by Microbes. Franz Schardinger (*Centr. Bakt. Par.*, 1911, ii, 29, 188—197).—Certain micro-organisms convert starch paste into substances soluble in water closely resembling dextrins. *Bacillus macerans* renders potato-starch completely soluble, arrowroot-starch nearly completely so, but has far less effect on rice and wheat starch. Part of the dextrin formed, about 25—30% of the starch taken, is crystalline, the rest being amorphous and gum-like. Two different crystalline dextrins distinguished as α and β have been

obtained from all four varieties of starch, the α-isomeride predominating. It crystallises in colourless, hexagonal plates or lance-shaped needles, and is doubly refractive, $[\alpha]_D$ +128°; the coloration of the crystalline precipitate with iodine is blue in thin layers when wet, greyish-green when dry. The β-isomeride crystallises in reniform aggregates of rhombic crystals, $[\alpha]_D$ +136°; the crystalline precipitate with iodine is a reddish-brown both wet and dry; it sinters and decomposes at 260°.

Both dextrins are precipitated from aqueous solution by alcohol, ether, chloroform, and iodine solution; they do not reduce Fehling's solution, and are not fermented by yeast. E. F. A.

Tellurium. ALEXANDER GUTBIER and FERDINAND FLURY (*J. pr. Chem.*, 1911, [ii], 83, 145—163. Compare Abstr., 1907, ii, 255).—The majority of the results recorded by previous investigators on the tellurichlorides and the telluribromides of the alkali metals and of aliphatic ammonium compounds have been confirmed; the existence of Rammelsberg's compounds, $8KCl,3TeCl_4$ and $8NH_4Cl,3TeCl_4$, and of the hydrated potassium tellurichloride described by von Hauer and by Wheeler (Abstr., 1893, ii, 457) is denied.

The salts described below are prepared by mixing an excess, generally one half to three-quarters, of a solution of carefully purified tellurium dioxide in the halogen acid with a solution of the alkali or substituted ammonium halide; with suitably selected concentrations, the desired salt crystallises more or less rapidly and is recrystallised from the dilute halogen acid. The tellurium is estimated by Lenher and Homberger's process (Abstr., 1908, ii, 428). The salts are characterised by their splendid colour and crystalline well, generally in the regular system. They dissolve without decomposition in a small quantity of water at the ordinary temperature or by gentle warming, but are extensively decomposed by even a small excess of water with the separation of tellurous acid. The telluribromides are stable in the air.

[With H. MICHELER.]—The following salts have been obtained: Ammonium tellurichloride is prepared best from dilute solutions and by spontaneous evaporation; it crystallises in sulphur-yellow octahedra. *Trimethylammonium tellurichloride*, $2NMe_3,H_2TeCl_6$, pale yellow needles; *diethylammonium*, $2NHEt_2,H_2TeCl_6$, sulphur-yellow, monoclinic crystals: *triethylammonium*, $2NEt_3,H_2TeCl_6$, yellow needles; *propylammonium*, $2NH_2Pr^{\alpha},H_2TeCl_6$, yellow, rhombic plates; *isopropylammonium*, $2NH_2Pr^{\beta},H_2TeCl_6$, greenish-yellow, monoclinic plates; *dipropylammonium*, $2NHPr^{\alpha}_2,H_2TeCl_6$, yellow, rhombic (or tetragonal) crystals; *butylammonium*, $2C_4H_9{\cdot}NH_2,H_2TeCl_6$, long, pale yellow needles; *isobutylammonium*, $2C_4H_9{\cdot}NH_2,H_2TeCl_6$, like the preceding salt. *Diethylammonium telluribromide*, $2NHEt_2H_2TeBr_6$, orange-red needles; *triethylammonium*, $2NEt_3{\cdot}H_2TeBr_6$, orange-red, monoclinic crystals; *propylammonium*, $2NH_2Pr^{\alpha},H_2TeBr_6$, orange-red plates; *isopropylammonium*, $2NH_2Pr^{\beta},H_2TeBr_6$, orange-red, tetragonal needles; *dipropylammonium*, $2NHPr_{\alpha_2},H_2TeBr_6$, orange-red, monoclinic plates; *butylammonium*, $2C_4H_9{\cdot}NH_2,H_2TeBr_6$, orange-red needles; *isobutylammonium*, $2C_4H_9{\cdot}NH_2,H_2TeBr_6$, orange-red plates. C. S.

Salts of Pertitanic Acid with Organic Bases. EDUARD KUNOWSKI and L. NISSENMANN (*Ber.*, 1911, 44, 224—229).—The authors describe the preparation and properties of a number of salts of pertitanic acid with primary and secondary aliphatic amines. The method of preparation adopted consists in the gradual addition of a mixture of the amine and 30% hydrogen peroxide to titanium trioxide and subsequent precipitation of the salt by the addition of a mixture of alcohol and ether, the temperature being maintained at $-10°$ to $-15°$.

The salts are all unstable, dissolve in water with a green colour, and decompose rapidly at the ordinary temperature. They dissolve in dilute sulphuric acid with the formation of hydrogen peroxide.

The *methylamine* salt, $(NH_3Me\cdot O)_2TiO_4,3H_2O$, has a yellowish-green colour; when exposed to the air it forms oily drops, and then decomposes with the liberation of carbon.

The *ethylamine* salt, $NH_3Et\cdot O\cdot TiO_4H,1\frac{1}{2}H_2O$, is a yellow powder.

The *propylamine* salt, $2NH_3Pr^{\alpha}\cdot O\cdot TiO_4H,H_2O_2,2H_2O$, has a yellowish-green colour; a second less stable salt has also been obtained.

Of the salts with secondary aliphatic amines, only the *diethylamine* salt, $2NH_2Et_2\cdot O\cdot TiO_4H,H_2O_2,14H_2O$, was obtained in a pure condition; it is a yellow powder.

The *dimethylamine* and *dipropylamine* salts so readily decompose that their composition has not been determined.

Attempts to prepare salts of pertitanic acid with tertiary amines and also with aniline were unsuccessful. F. B.

Ruthenihalides. ALEXANDER GUTBIER [with G. A. LEUCHS] (*Ber.*, 1911, 44, 306—308).—The following compounds were prepared according to a method previously described (Abstr., 1907, i, 289):

Triethylammonium ruthenichloride, $(NHEt_3)_2RuCl_6$, forms large, broad, blackish-red plates. *Triethylammonium ruthenibromide*, $(NHEt_3)_2RuBr_6$, crystallises in large, black plates. iso*Propylammonium ruthenichloride*, $(NH_3Pr^{\beta})_2RuCl_6$, forms glistening, dark greenish-brown or black needles. iso*Propylammonium ruthenibromide*, $(NH_3Pr^{\beta})_2RuBr_6$, is obtained in dark bluish-black needles. n-*Butylammonium ruthenichloride*, $(C_4H_9\cdot NH_3)_2RuCl_6$, forms dark, greenish-brown, glistening needles. n-*Butylammonium ruthenibromide*, $(C_4H_9\cdot NH_3)_2RuBr_6$, forms deep bluish-black needles. *Benzylammonium ruthenichloride*, $(C_7H_7\cdot NH_3)_2RuCl_6$, crystallises in greenish-brown, slender needles. *Benzylammonium ruthenibromide*, $(C_7H_7\cdot NH_3)_2RuBr_6$, forms black, felted needles. *Pyridinium ruthenichloride*, $(C_5H_6N)_2RuCl_6$, forms brown needles *Pyridinium ruthenibromide*, $(C_5H_6N)_2RuBr_6$, crystallises in light bluish-black needles. *α-Picolinium ruthenichloride*, $(C_5NH_5Me)_2RuCl_6$, is obtained in small, bronze-coloured leaflets. *α-Picolinium ruthenibromide*, $(C_5NH_5Me)_2RuBr_6$, forms shining, bluish-black needles.

T. S. P.

Labile Hydrated Forms Fixed by means of an Organic Base. GIUSEPPE A. BARBIERI and F. CALZOLARI (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 584—590).—The authors have acted on various metallic salts in aqueous solution with hexamethylenetetramine, and on the hypothesis that this substance combines with hydrates already existing in the solution, the composition of the solid substances which separate yields information as to the nature of the hydrates in question (compare Kurnakoff, Abstr., 1898, ii, 475). The following facts accord with the supposition that the hexamethylenetetramine is not united with the metallic atom, but is added to the molecule of the hydrated salt present in the solution: (1) anhydrous cobalt chloride forms with hexamethylenetetramine a compound in which the base is attached to the metal, and this compound is blue; (2) a compound, $(AcONa,3H_2O)_2C_6H_{12}N_4$, exists, and it is not probable that the base could be attached to sodium; (3) with salts which usually are anhydrous, or give hydrates containing little water, hexamethylenetetramine compounds are obtained which contain little or no water. The compounds described are, therefore, to be regarded as amines of hydrated salts.

The following compounds are prepared by acting on concentrated (20%) aqueous solutions of the chlorides, bromides, and iodides of magnesium, manganese, cobalt, and nickel with concentrated aqueous solutions of hexamethylenetetramine (2—4 mols.). They form large, measurable crystals, which are not deliquescent. The tendency to effloresce in contact with dehydrating agents is greatest in the case of the chlorides, least with the iodides, which are stable to air and light. In solution, the manganese derivatives gradually deposit manganous hydroxide. The *compound*, $MgCl_2,10H_2O,2C_6H_{12}N_4$, forms colourless, transparent, tabular crystals belonging to the triclinic system (holosymmetric):

$[a:b:c=0{\cdot}8321:1:0{\cdot}8573;\ \alpha=125°43',\ \beta=50°21',\ \gamma=123°56']$.

The *compound*, $MnCl_2,10H_2O,2C_6H_{12}N_4$, forms minute crystals of a pale flesh colour. The *compound*, $CoCl_2,10H_2O,2C_6H_{12}N_4$, crystallises in reddish-violet laminæ, which in contact with phosphoric oxide lose all their water and become intensely blue. The *compound*,

$NiCl_2,10H_2O,2C_6H_{12}N_4$,

crystallises in green laminæ, which on dehydration in an oven become first yellow, then violet. The *compound*,

$MgBr_2,10H_2O,2C_6H_{12}N_4$,

forms plates which are almost square; they belong to the monoclinic system (holosymmetric): $[a:b:c=0{\cdot}9022:1:0{\cdot}5111;\ \beta=90\ 40']$. The *compound*, $MnBr_2,10H_2O,2C_6H_{12}N_4$, forms almost colourless crystals. The *compound*, $CoBr_2,10H_2O,2C_6H_{12}N_4$, forms reddish-violet crystals. The *compound*, $NiBr_2,10H_2O,2C_6H_{12}N_4$, crystallises in green laminæ. The *compound*, $MgI_2,10H_2O,2C_6H_{12}N_4$, forms long, colourless, transparent crystals, which belong to the monoclinic system (holosymmetric): $[a:b:c=0{\cdot}8802:1:0{\cdot}495;\ \beta=90°1']$. The *compound*,

$MnI_2,10H_2O,2C_6H_{12}N_4$,

is a white powder. The *compound*, $CoI_2,10H_2O,2C_6H_{12}N_4$, forms rose-coloured, tabular crystals. The *compound*,

$NiI_2,10H_2O,2C_6H_{12}N_4$,

forms emerald-green crystals. In some cases where the analytical results do not permit of the exact determination of the amount of contained water, the question can be settled from relations of isomorphism and power to form mixed crystals which exist between many of the substances. The crystallographic measurements were executed by E. Billows. R. V. S.

Alkylation of Acid Amides. Motooki Matsui (*Mem. Coll. Sci. Eng. Kyoto*, 1910, 2, 397—400).—In the alkylation of amides, silver oxide may be replaced by cuprous oxide, lead oxide, or anhydrous potassium carbonate.

When a mixture of acetamide and ethyl iodide is heated for three to four hours on the water-bath with one of these substances, ethyl iminoacetate is produced. Benzamide, under the same conditions, yields ethyl iminobenzoate.

It is therefore highly probable that in alkylating with silver oxide and an alkyl iodide, the silver oxide accelerates the reaction merely by the removal of the hydriodic acid produced, and not by the intermediate formation of a silver derivative (compare Lander, Trans., 1900, 77, 729).

The author considers it probable that the formation of imino-esters by the action of methyl sulphate on amides is due to the direct alkylation of the enolic form: NH:CR·OH, and not to the addition of methyl sulphate to the ketonic form, as suggested by Bühner (Abstr., 1904, i, 882). F. B.

Formation and Decomposition of Calcium Cyanamide. Max Le Blanc and M. Eschmann (*Zeitsch. Elektrochem.*, 1911, 17, 20—34).—It is shown that the reaction $CaC_2 + N_2 \rightleftarrows CaCN_2 + C$ is reversible. The equilibrium pressure of nitrogen, however, is dependent on the quantity of nitrogen which has been taken up by the carbide. Measurements of the pressures are made at 1200° and 1300°. After almost saturating a quantity of carbide with nitrogen, successive quantities of nitrogen are removed from it by diminishing the pressure, and the corresponding equilibrium pressures are measured; the quantity of combined nitrogen is then increased by adding fresh nitrogen, and the pressures again measured. The two curves do not agree with each other, the pressure corresponding with a given percentage of combined nitrogen constantly decreases with the duration of the experiments; apparently the cyanamide becomes more stable. A careful chemical examination of the reaction shows that the reversible formation of calcium cyanamide is really the reaction being observed, but the calcium cyanamide gradually volatilises out of the mixture and condenses in the cooler parts of the apparatus, where it can no longer decompose, partly owing to the lower temperature and partly owing to the absence of carbon. T. E.

Some Solid Ammoniates. Carlo Gastaldi (*Gazzetta*, 1910, 40, ii, 475—481).—When a concentrated aqueous solution of potassium ferricyanide is added to an ammoniacal solution of silver nitrate, a fine-grained, deep red, crystalline precipitate is deposited, which has the

composition $2[Ag_3Fe(CN)_6],5NH_3$. By varying the conditions, the substance can be obtained as an amorphous, flocculent precipitate, or, by dissolving freshly precipitated silver ferricyanide in ammonia and evaporating the solution at the ordinary temperature, in large crystals. In all cases the composition is the same. When the ammonia is replaced by methylamine or ethylamine, *methyl-* and *ethyl-ammoniates* of similar composition are obtained.

The qualitative test for the ferricyanic radicle may be masked by the presence of simple cyanides in a solution under investigation. If aluminium and hydrochloric acid are added to the liquid, however, the production of a coloration with an iron salt will indicate the presence of a ferricyanide, for in these circumstances the formation of the complex from a cyanide and the iron salt cannot occur. R. V. S.

Action of Hydroxylamine on Nitrosochlorides and Nitrosates. III. αβ-Amylenehydroxylamineoxime and Derivatives. GUIDO CUSMANO (*Gazzetta*, 1910, **40**, i, 525—536. Compare Abstr., 1910, i, 863).—*β-Hydroxylamino-β-methylbutan-γ-oneoxime* (*amylenehydroxylamineoxime*), $OH\cdot NH\cdot CMe_2\cdot CMe{:}N\cdot OH$, is prepared by suspending amylene nitrosate in a mixture of methyl alcohol and ether containing hydroxylamine (2 mols.). The reaction commences on warming, and then proceeds spontaneously. After removal of the solvent, the residue is dissolved in a little water and treated with sodium carbonate to dissolve the hydroxylamine nitrate present, and from the solution β-hydroxylamino-β-methylbutan-γ-oneoxime crystallises out on cooling. It forms rhombohedra, or laminar, hexagonal prisms, m. p. about 112° (previously softening), and reduces Fehling's solution readily in the cold. The *hydrochloride*, $C_5H_{12}O_2N_2,HCl$, forms clusters of crystalline leaflets, m. p. 125—130°, and are very deliquescent. The *nitroso-oxime* is obtained as an oil of a blue tinge by oxidising the hydroxylamino-oxime with the calculated quantity of permanganate. The p-*nitrobenzylidene* derivative, $OH\cdot N{:}C_5H_9\cdot \underset{\diagdown O \diagup}{N{-}C}\cdot C_6H_4\cdot NO_2$ (from *p*-nitrobenzaldehyde), forms pale yellow, hexagonal laminæ, m. p. about 187°. It dissolves in alkalis, producing a red coloration.

β-Hydroxylamino-β-methylbutan-γ-oneoxime reacts readily with nitrous acid, yielding *β-nitrosohydroxylamino-β-methylbutan-γ-oneoxime*, $OH\cdot N(NO)\cdot CMe_2\cdot CMe{:}N\cdot OH$, which is a very stable substance, crystallising in long, colourless needles, m. p. 81—82°. It does not reduce Fehling's solution, but yields a bluish-green coloration with a solution of phenol in sulphuric acid. It can be boiled with water without suffering decomposition, but it is readily decomposed by dilute acids even in the cold. It dissolves in sodium carbonate with effervescence, and the solution on concentration yields the *sodium* salt of the *iso*nitroamine. The *iso*nitroamine can displace nitrous acid, so that this sodium salt can be prepared by mixing concentrated solutions of hydroxylamino-oxime and sodium nitrite in the presence of a little sulphuric acid. It crystallises with $3H_2O$, which it loses at 116°. The *anhydrous* salt, $C_5H_{10}O_3N_3Na$, has m. p. 130° (decomp.).

β-Hydroxylamino-β-methylbutan-γ-oneoxime, when kept in an alcoholic ethereal solution saturated with hydrogen chloride, eventually deposits

a hydrochloride, $C_5H_{11}O_2N,HCl$, in tufts of long, acicular crystals, m. p. 145° (decomp.), which are not deliquescent. On treatment with sodium carbonate, a base is obtained, crystallising in long, colourless prisms, m. p. 96—98°. This base readily reduces Fehling's solution in the cold. To it is ascribed the constitution of *β-hydroxylamino-β-methylbutan-γ-one*, $OH\cdot NH\cdot CMe_2\cdot COMe$, and this is confirmed by the existence of a *p*-nitrobenzylidene derivative, $C_{12}H_{14}O_4N_2$, which crystallises in yellow, rectangular tablets, decomposing at 176°.

If hydroxylaminomethylbutanoneoxime is dissolved in concentrated alkali, and the solution after some days is treated with carbon dioxide, a precipitate is obtained, from which two substances can be isolated. One crystallises in small, colourless prisms, m. p. 96—100°, and from its composition and properties is *β-hydroxy-β-methylbutan-γ-oneoxime*, $OH\cdot CMe_2\cdot CMe:NOH$. The other *compound* forms long, colourless prisms, m. p. 184° (decomp.).

To explain the differences between the hydroxylamino-oximes of pinene and amylene and that of limonene, it is suggested that the two first, being saturated compounds, exist solely, or chiefly, as *trans*-forms, whilst the unsaturated limonene compound can also assume the labile *cis*-form. R. V. S.

Unsaturated Lead Alkyls. JULIUS TAFEL (*Ber.*, 1911, **44**, 323—337).—In his electrolytic experiments on organic substances with mercury or lead cathodes, the author has frequently observed the formation of small quantities of oily products; with lead cathodes the oil is red. At his suggestion, Renger (following abstract) has studied the formation of these oily products, and has obtained the red oil in larger quantities from acetone; he considers that it consists essentially of lead tetra-*iso*propyl, since lead di-*iso*propyl dibromide is produced from it by the action of bromine. Since the lead tetra-alkyl compounds are colourless and the formation of a di-alkyl compound from a tetra-alkyl has hitherto been unknown, the author has extended the investigation of these oils.

The apparatus consists of a glass cathodic vessel shaped like a separating funnel and provided with a closely fitting lead cover, through apertures in which are fitted a thermometer, an inlet-tube for the delivery of carbon dioxide into the cathodic compartment, and the porcelain anodic cell. The cathode consists of six strips of lead, and the anode of a lead cylinder. The anodic liquor is 20% sulphuric acid; the cathodic solution is a mixture of 20% sulphuric acid and acetone (in the case of higher ketones a little alcohol must also be added). The temperature is kept at 45—50°, and the cathodic current density at about 0·5 amp./sq. cm. During the experiment the cathodic solution is well agitated by a current of carbon dioxide, and the red oil collects together with a white precipitate at the bottom of the vessel. It is run out into an apparatus (figured and described), in which it can be washed with dilute potassium hydroxide and with water, dried over sodium sulphate, and filtered, all of the operations being performed with the exclusion of air. The purified product is a viscous oil with the colour of bromine and an unpleasant odour. It loses its red colour rapidly in the light, leaving a golden-yellow oil consisting

chiefly of lead tetra-*iso*propyl. When rapidly heated, the red oil decomposes at 150° with separation of finely divided lead; it decomposes at 85° in a vacuum. In contact with oxygen, the oil becomes coated with a yellowish-brown, strongly alkaline skin. When a solution of the red oil in an indifferent solvent is treated with oxygen, it acquires a pale yellow colour, and after filtration contains lead tetra-*iso*propyl and lead di-*iso*propyl oxide; the latter is extracted with dilute acetic acid, and is isolated in the form of *lead di-iso*propyl *dibromide*, $PbPr^{\beta}Br_2$. This salt, which crystallises in felted needles and decomposes when kept, even in darkness, is also obtained by carefully treating the red oil in well-cooled ether or ethyl acetate with bromine until the latter only slowly disappears. The corresponding *dichloride*, *dinitrate*, and *chromate* are described. When the oxidised filtered solution of the red oil is distilled at 40° in a vacuum, and the yellowish residue, which exhibits the properties of lead tetra-*iso*propyl, is triturated with concentrated hydrochloric acid, *lead tri-*iso*propyl chloride*, $PbPr^{\beta}_3Cl$, is obtained. It has a very unpleasant odour, is more volatile with steam, and is less stable than the dichloride. The corresponding *iodide* is described. The author is of opinion that the red oil consists essentially of lead tetra-*iso*propyl together with about 20% of lead di-*iso*propyl, to which the colour is due.

Pure lead tetra-*iso*propyl has not been obtained on account of its great instability, but the behaviour of lead tetra-ethyl is quite analogous to that of the red oil mentioned above; thus with bromine (1 mol.) in well-cooled ether or ethyl acetate it yields *lead triethyl bromide*, $PbEt_3Br$, which crystallises in large, colourless needles, and has an unpleasant odour; with 2 mols. of the halogen, lead tetra-ethyl yields *lead diethyl dibromide*, $PbEt_2Br_2$, the properties of which are quite analogous to those of the di-*iso*propyl dibromide.

C. S.

Lead Alkyl Compounds from Methyl Ethyl Ketone and Diethyl Ketone. Georg Renger (*Ber.*, 1911, **44**, 337—338. Compare preceding abstract).—The electrolytic reduction of methyl ethyl ketone and of diethyl ketone (in the presence of alcohol) at lead cathodes proceeds in a manner quite analogous to that of acetone. The resulting red oils have been characterised by chlorination and bromination in chloroform or ether, whereby the following salts, which are even more unstable than the *iso*propyl compounds, have been obtained. *Lead tri-*sec.*-butyl chloride*, $Pb(C_4H_9)_3Cl$, forms pale yellow needles, has an unpleasant odour, and melts and suddenly explodes at about 130° when heated rapidly. *Lead di-*sec.*-butyl bromide*, $Pb(C_4H_9)_2Br_2$, crystallises in yellow needles. *Lead di-γ-amyl dibromide*, $Pb(C_5H_{11})_2Br_2$, obtained from the oil from diethyl ketone, forms extremely unstable, brownish-yellow crystals.

C. S.

Constitution of Copper Acetylide. II. Johannes Scheiber and Hans Reckleben [and, in part, K. Strauss] (*Ber.*, 1911, **44**, 210—223. Compare Scheiber, Abstr., 1908, i, 933).—Further experi-

ments have confirmed the existence of copper acetylide in the hydrated form C_2Cu_2,H_2O, and in the anhydrous form C_2Cu_2.

The fact that when the acetylide is decomposed by mild chemical reagents, for example, hydrogen sulphide and potassium cyanide, quantitative yields of acetylene are obtained, points to the conclusion that its constitution must be closely related to that of acetylene. No indication of the conversion of the hydrate into an aldehyde derivative has been observed, either by leaving in contact with water or ammonia, by drying, or under the influence of substances which may be present during its formation.

The structural formulæ of the compounds depend on that of acetylene. According to Nef's scheme, the anhydrous compound would be $Cu_2C{:}C{:}$, and the hydrate, $Cu_2C{:}C\cdots OH_2$.

The black carbonaceous material usually obtained when copper acetylide is decomposed is shown to be due to oxidation; if oxygen or oxidising substances are excluded during the preparation and decomposition of the acetylide, no carbonaceous residue is obtained. If, on the other hand, the water used contains dissolved air, or if the pure carbide is heated in an atmosphere of carbon dioxide at 100°, or if oxidising agents, such as cupric or ferric salts, are used for washing the acetylide, appreciable amounts of black residue are obtained (compare Söderbaum, Abstr., 1897, i, 309). Analyses of the carbonaceous compound agree with the formulæ $(C_{11}H_6O_3)_x$ for the product when dilute hydrochloric acid is used, and $(C_{11}H_5O_3)_2$ for the product when concentrated acid is used.

The detection by means of acetylene of copper in solutions of ammoniacal cupric salts reduced by means of hydroxylamine can be carried out at a dilution of 1 in 1,100,000, or in the presence of large quantities of ammonium acetate or tartrate, of 1 in 200,000.

J. J. S.

Sulphonation of Benzene. Robert Behrend and Martin Mertelsmann (*Annalen*, 1911, 378, 352—365).—The sulphonation of benzene by pure, concentrated sulphuric acid at 240—250° results almost exclusively in the formation of the *m*-disulphonic acid, less than 1% of the para-isomeride being produced after one and a-half-hours' heating. The addition of a little mercury causes the formation of the *m*- and the *p*-disulphonic acids in the proportion 2 : 1; ferrous sulphate acts similarly, about 10% of benzene *p*-disulphonic acid being produced. The two acids are readily separated in the form of their sodium salts, since sodium benzene-*p*-disulphonate is practically insoluble in a concentrated solution of sodium benzene-*m*-disulphonate.

The two acids are interconvertible by heating with concentrated sulphuric acid and a little mercury at 240—250°, an equilibrium mixture of about 2 parts of the *m*-disulphonic acid and 1 part of the para-isomeride being formed; the same result is attained, but extremely slowly, in the absence of the mercury.

The sodium salts of both acids, by treatment with pure concentrated sulphuric acid at 240—250°, are converted into benzene-1 : 3 : 5-trisulphonic acid, which is also formed to some extent by heating benzene

with concentrated sulphuric acid and potassium pyrosulphate at 240—250°. C. S.

Action of Strong Tertiary Bases on Sulphonyl Chlorides. EDGAR WEDEKIND and D. SCHENK (*Ber.*, 1911, 44, 198—202).—Triethylamine reacts with sulphonyl chlorides when dissolved in indifferent solvents, for example, benzene, provided a hydrogen atom is attached to the α-carbon atom with respect to the sulphonyl group. Hydrogen chloride is eliminated as in the case of the chlorides of carboxylic acids (Abstr., 1906, i, 437; 1909, i, 459), but the phenylsulphens, for example, $CHPh{:}SO_2$, cannot be isolated. With benzylsulphonyl chloride, stilbene is obtained by the elimination of sulphur dioxide and the union of the two CHPh: groups.

The chlorides of aromatic sulphonic acids do not react with tertiary bases.

Diphenylmethanesulphonic acid, $CHPh_2{\cdot}SO_3H,1{\cdot}5H_2O$, crystallises from benzene in hygroscopic needles, m. p. 94—96°; when fused with potassium hydroxide, it yields *p*-hydroxydiphenylmethane (Trans., 1882, 41, 34), and when heated with water at 240° for eight hours, it yields diphenylmethane. The acid chloride has not been prepared. Sodium sulphite solution and ω-chlorodiphenylmethane at 120—125° yield *benzhydrol ether*, $C_{26}H_{22}O$, m. p. 109°. J. J. S.

Phenanthrene-2-sulphonic Acid and Some of its Derivatives. HÅKAN SANDQVIST (*Annalen*, 1911, 379, 79—90).—The phenanthrene-2-sulphonic acid used in the experiments is obtained in the form of the potassium salt from the by-products of the sulphonation of phenanthrene by Kunz's process. The acid is prepared from the acid chloride and water at 130—135°, from the barium salt and sulphuric acid, or from the lead salt and hydrogen sulphide. The acid contains H_2O, has m. p. about 150°, and is freed from its solvents only with difficulty; its electrical conductivity does not differ much from that of the 3-sulphonic acid (Abstr., 1909, i, 779). The following salts are described, the solubilities being expressed as before (*loc. cit.*): potassium ($\frac{1}{2}H_2O$), sol. 0·275; ammonium, sol. 0·37; *sodium* ($\frac{1}{2}H_2O$), white leaflets or needles, sol. 0·42; *calcium*, sol. 0·024; barium ($\frac{1}{2}H_2O$), sol. 0·016; *magnesium* ($6H_2O$), elongated leaflets, sol. 0·051; *zinc* ($6H_2O$), sol. 0·083; ferrous ($5H_2O$), sol. 0·044; lead (H_2O), sol. 0·014; *copper* (H_2O), bluish-green crystals, sol. 0·25; *silver*, sol. 0·099. *Phenanthrene-2-sulphonyl chloride*, obtained from the potassium salt and phosphorus pentachloride, has m. p. 156°, is oxidised by acetic and chromic acids to *phenanthraquinone-2-sulphonyl chloride*, yellow leaflets or needles, m. p. 245—246° (decomp.), and forms a *sulphonamide*, m. p. 253—254°, and *sulphonanilide*, $C_{14}H_9{\cdot}SO_2{\cdot}NHPh$, m. p. 157—158°, by the usual methods.

Methyl phenanthrene-2-sulphonate is dimorphous, the stable modification forming rhombic plates, the labile modification leaflets. The fact that many derivatives of phenanthrene have two m. p.'s may be due to dimorphism; the preceding ester, crystallised from methyl alcohol, has m. p. 92·5—93° and 101·5°, whilst in a capillary tube the m. p. is either 85°, 98°, or 101·5°. By oxidation with chromic

id acetic acids the ester yields *methyl phenanthraquinone-2-sulphon-*
e, yellow leaflets, m. p. 196—197°, or elongated leaflets, m. p.
2—192·5°. *Ethyl phenanthrene-2-sulphonate* has m. p. 88·5°.

C. S.

An Organo-metallic Compound of the Aniline Series. KATTENBURY HODGES (*Chem. News*, 1910, 103, 52).—By slow dition of zinc chloride solution to a saturated aqueous solution of, iline, slender, colourless, highly refractive crystals of a compound of nc chloride with aniline chloride were obtained. N. C.

Osmichlorides. ALEXANDER GUTBIER [with P. WALBINGER] (*Ber.*, 11. 44, 308—312).—The following osmichlorides were prepared by teraction of sodium osmichloride (Abstr., 1910, ii, 45) and aryl bstituted ammonium chlorides. They were purified by recrystallisa-n from dilute hydrochloric acid; the aqueous solutions undergo composition. The salts are all anhydrous and stable in the air. *Phenylammonium osmichloride*, $(NH_3Ph)_2OsCl_6$, forms brownish-red, mbic leaflets. *Phenylmethylammonium osmichloride*, $(NH_3MePh)_2OsCl_6$, ms brownish-red, monoclinic crystals, showing pleochroism. *o-Tolyl-monium osmichloride*, $(C_6H_4Me\cdot NH_3)_2OsCl_6$, is obtained in yellow brownish-red, rhombic needles, which are pleochroic. *m-Tolyl-monium osmichloride* forms slender, pleochroic, brownish-red, rhombic dles. *p-Tolylammonium osmichloride* crystallises in yellowish-red, mbic, pleochroic leaflets. *o-4-Xylylammonium osmichloride*, $(C_6H_3Me_2NH_3)_2OsCl_6$, ms shining red, monoclinic needles. *m-4-Xylylammonium osmi-ride* forms strong, pleochroic, ruby-red, rhombic crystals. *p-5-lylammonium osmichloride* is obtained in red, rhombic, pleochroic dles. *Pyridinium osmichloride*, $(C_5H_6N)_2OsCl_6$, forms red, rhombic tes. *α-Picolinium osmichloride*, $(C_5NH_5Me)_2OsCl_6$, forms yellowish-, rhombic leaflets. *Quinolinium osmichloride*, $(C_9NH_8)_2OsCl_6$, is ained in yellowish-red, feebly pleochroic, monoclinic needles. *Benzyl-monium osmichloride*, $(C_7H_7\cdot NH_3)_2OsCl_6$, forms brownish-red, mono-ic plates. *α-Naphthylammonium osmichloride*, $(C_{10}H_7\cdot NH_3)_2OsCl_6$, stallises in brownish-red, pleochroic, rhombic needles. *β-Naph-lammonium osmichloride* forms brownish-red, pleochroic, rhombic lets. T. S. P.

actyl Compounds of Primary Aromatic Amines. KARL S (*J. pr. Chem.*, 1911, [ii], 83, 1—21) [with K. SINNER.]—The ylation of several primary aromatic amines has been studied ntitatively at about 100° by heating mixtures of the amine and ic acid, with or without water, in a water-bath and titrating the hanged acid after definite intervals of time, phenolphthalein being l as indicator. In the experiments without water, the lactate he amine is used. The results, which are expressed graphically, v that the formation of the lactyl compound is retarded by the ence of water, but is facilitated, contrary to Menschutkin's rience in the case of acetanilide, by using an excess of the amine luidine).

The lactylation of different amines under the same conditions, namely, 1 mol. of base, 1 mol. of acid, and 1·66 mols. of water at 160°, shows that the reactivity of the amino-group in aniline is affected slightly by the presence of a methyl group in the para-position, considerably and unfavourably by methyl in the ortho-position, and favourably by the ethoxy-group in the para- and still more so in the ortho-position.

[With Fr. Mette.]—Lactophenin in glacial acetic acid at 0° is converted by nitric acid, D 1·40, into 2-*nitro*-4-*ethoxylactanilide* (2-*nitrolactophenin*), $OEt\cdot C_6H_3(NO_2)\cdot NH\cdot CO\cdot CHMe\cdot OH$, yellow needles or leaflets, m. p. 112°, the position of the nitro-group being determined by the fact that the substance and nitrophenacetin give the same nitrophenetidine by hydrolysis. Nitric acid, D 1·40, converts powdered lactophenin into 2 : 6-*dinitroethoxylactanilide*, yellow needles or leaflets, m. p. 135°, which yields the known dinitrophenacetin by hydrolysis and treatment of the product with acetic anhydride. Concentrated sulphuric and nitric acids at 0° convert dinitrolactophenin into the *nitrate*, $OEt\cdot C_6H_2(NO_2)_2\cdot NH\cdot CO\cdot CHMe\cdot ONO_2$, yellow leaflets, m. p. 192° (decomp.), which yields dinitrophenetidine, amongst other products, by hydrolysis with dilute alcoholic potassium hydroxide.

[With A. Schuster.]—3-*Nitrolacto*-p-*toluidide*,

$$NO_2\cdot C_6H_3Me\cdot NH\cdot CO\cdot CHMe\cdot OH,$$

yellow needles, m. p. 86—87°, obtained from an acetic acid solution of lacto-*p*-toluidide and nitric acid, D 1·48, at 0°, yields 3-nitro-*p*-toluidine by hydrolysis. 3 : 5-*Dinitrolacto*-p-*toluidide*, yellow needles, m. p. 139—140°, obtained from the preceding compound and concentrated nitric and sulphuric acids at 0°, yields 3 : 5-dinitro-*p*-toluidine by hydrolysis. The *nitrate*, $C_6H_2Me(NO_2)_2\cdot NH\cdot CO\cdot CHMe\cdot ONO_2$, white needles, decomp. 160°, obtained from lacto-*p*-toluidide and concentrated sulphuric acid and nitric acid, D 1·48, at 0°, also yields 3 : 5-dinitro-*p*-toluidine by hydrolysis.

Owing to the ease with which lactotoluidides are hydrolysed even by dilute alkali, the electrolytic reduction of 3-nitrolacto-*p*-toluidide must be effected in an approximately neutral solution which is slightly alkaline in the immediate neighbourhood of the cathode. Even then the reduction does not proceed smoothly, for with an anodic liquid consisting of cold saturated sodium carbonate and a cathodic solution of acetic acid and sodium acetate, and a cathodic current density of 3—3·5 amperes per sq. dcm., the nitrolactotoluidide yields a number of products, from which 3 : 3′-*azoxylacto*-p-*toluidide*,

$$ON_2(C_6H_3Me\cdot NH\cdot CO\cdot CHMe\cdot OH)_2,$$

yellow needles or leaflets, m. p. 234° (decomp.), is isolated. By hydrolysis by dilute alcoholic potassium hydroxide, it yields 3 : 3′-azoxy-*p*-*toluidine*, red needles, m. p. 188°, which is converted by electrolytic reduction in sulphuric acid into the sparingly soluble sulphate of 3 : 4-tolylenediamine. The electrolytic reduction of 3-nitrolacto-*p*-toluidide in acid solution by Bochringer's process yields, amongst other products, acetaldehyde and 40—60% of 5-*methylbenziminazolone*,

$$C_6H_3Me\langle\begin{matrix}NH\\NH\end{matrix}\rangle CO,$$

white crystals, m. p. 292—295° (*acetyl* derivative, m. p. 176°), the

nstitution of which is proved by the formation of the same substance om 3 : 4-tolylenediamine and carbamide.

[With Fr. Mette and A. Schuster.]—The electrolytic reduction of nitroethoxylactanilide in approximately neutral (cathodic) solution the b. p. yields 2 : 2′-*azoethoxylactanilide*,

$$N_2[C_6H_3(OEt)\cdot NH\cdot CO\cdot CHMe\cdot OH]_2,$$

llowish-red needles, m. p. 269°, in 15—20% yield. By hydrolysis the o-compound yields *azo-p-phenetidine*, m. p. 143°, which forms an etyl derivative, m. p. 306°, identical with the azophenacetin obtained the electrolytic reduction of nitrophenacetin.

The electrolytic reduction of 2-nitroethoxylactanilide in acid lution yields acetaldehyde, several unidentified products, one of hich has m. p. 161°, and ethoxybenziminazolone (Cohn, Abstr., 1899, 944), the *diacetyl* derivative of which has m. p. 163°. C. S.

The Solubility of Sodium Picrate in Solutions of Sodium alts. Woldemar Fischer and P. Miloszewski (*Chem. Zentr.*, 1910, 1048; from *Kosmos*, 1910, **35**, *Radziszewski-Festband*, 538—542). The solubility of sodium picrate in aqueous solutions of sodium, rbonate, chloride, sulphate, phosphate, nitrate, bromide, and hydroide of various strengths at 25° was determined. The measurements ve proved that, contrary to the statement of Reinhard (*Zeitsch. anal. hem.*, 1910, **49**, 269), the solubility of sodium picrate is lowered by e presence of the sodium ions in accordance with the law of mass ction. N. C.

New Derivatives of Indene. Victor Grignard and Charles urtot (*Compt. rend.*, 1911, **152**, 272—274).—Organo-magnesium romides act on indene, giving rise to a sparingly soluble *magnesium denyl bromide*, $CH\ll^{C_6H_4}_{CH}\gg CH\cdot MgBr$. When treated in the usual ay, this yields the two following compounds: 1-*Indenol*, C_9H_8O, ellow prisms, m. p. 57—58°, b. p. 140°/10 mm., with partial ehydration. *Indene-1-carboxylic acid*, $CH\ll^{C_6H_4}_{CH}\gg CH\cdot CO_2H$, amois-coloured, prismatic needles, m. p. 161°.

Magnesium indenyl bromide reacts with fluorenone at 120° to give theoretical yield of tert.-1-*indenylfluorenol* (I):

$$\begin{array}{l} CH\cdot C_6H_4 \quad C_6H_4 \\ \| \quad\quad\quad | \\ CH\cdot CH \text{---} C(OH) \end{array} \gg C_6H_4 \qquad\qquad \begin{array}{l} CH\cdot C_6H_4 \\ \| \\ CH\cdot CH\cdot CPh_2\cdot OH \end{array}$$

(I.) (II.)

This compound crystallises in colourless needles, m. p. 151—152°. the same way, benzophenone gives 1-*indenyldiphenylcarbinol* (II), substance occurring in pale yellow tablets, m. p. 131—132°. A rtion of the carbinol undergoes dehydration during the preparation, rming *diphenylbenzfulvene*, $CH\ll^{C_6H_4}_{CH}\gg C{:}CPh_2$, orange-yellow angles, m. p. 111—112°. W. O. W.

Anthracene. I. Anthranol and Anthraquinol. Kurt H. eyer (*Annalen*, 1911, **379**, 37—73).—Dimroth's dianthrone and

Meyer's dianthranol (Abstr., 1909, i, 168), which are stable separately, not only in the solid state, but also in solution, and are mutually interconvertible only by energetic chemical means, are distinct isomerides, not tautomerides of the enol-keto-type, claimed by Thiele and by Baly for phenols of the benzene series. In the present paper the author shows that the monohydric and dihydric meso-phenols of the anthracene series, anthranol and anthraquinol, can each exist in two stable desmotropic forms.

The substance, long known as anthranol, reacts sometimes as a phenol, sometimes as a ketone; it is colourless, completely insoluble in cold aqueous alkalis, and its solutions generally are non-fluorescent. When its 5—10% solution in boiling sodium hydroxide is cooled rapidly to −5° and treated with cold 5% sulphuric acid, a new *substance*, $C_{14}H_{10}O$, is obtained, which crystallises in brownish-yellow leaflets, is easily soluble in cold aqueous alkalis, and forms solutions with an intense blue fluorescence; it sinters at 120° and melts completely at about 152°, but when placed in a bath previously heated to 120°, it melts at once. This substance is called anthranol, the name anthrone being reserved for the older substance. Anthranol changes into anthrone by keeping in a desiccator. The two substances attain a state of equilibrium when fused or dissolved, the change being easily followed by the formation or the disappearance of the blue fluorescence. Since both substances separately are stable for a long time in alcohol, it is possible to answer the question whether the activity of phenols is due to the enolic or to the keto-modification. In cold alcohol anthrone is not attacked by iodine, bromine, ferric chloride, or amyl nitrite; on boiling, however, particularly in solvents which cause a rapid transformation of anthrone into anthranol, reactions occur. In cold alcohol anthranol is attacked at once by bromine or iodine, and is oxidised to dianthrone by ferric chloride; also amyl nitrite in benzene at the ordinary temperature oxidises anthranol to dianthrone; dianthranol is never produced, not even when anthranol is oxidised by alkaline potassium ferricyanide. An alcoholic solution of anthranol at 25° couples readily with *p*-nitro*anti*diazobenzene hydrate to form Kaufler and Suchannek's anthraquinone-*p*-nitrophenylhydrazone; under similar conditions anthrone does not couple; also nitrosodimethylaniline condenses with anthranol, but not with anthrone, in alcoholic solution. Thus the reactivity of the hydroxylic modification supports Dimroth's results in connexion with the reactivity of enol-keto-tautomerides in the aliphatic series (Abstr., 1907, i, 662).

As is well known, anthraquinol (oxanthranol), obtained by reducing anthraquinone with zinc dust and alkali, forms brown leaflets, dissolves in cold aqueous sodium hydroxide to form a red disodium salt, yields solutions with an intense green fluorescence, and is rapidly oxidised to anthraquinone by iodine, bromine, or oxygen; its *dibenzoate* has m. p. 292°, and is non-fluorescent. Consequently anthranol is the true anthraquinol, $C_6H_4<\begin{matrix}C(OH)\\ \|\\ C(OH)\end{matrix}>C_6H_4$. It cannot be readily transformed into the keto-modification, *oxanthrone*,

$C_6H_4<\overset{CO}{\underset{CH(OH)}{}}>C_6H_4$, which is readily obtained, however, by hydrolysing bromoanthrone (Goldmann's bromoanthranol) by boiling 50% aqueous acetone (see also following abstract). Oxanthrone, m. p. 167°, forms yellow, almost colourless needles, gives colourless solutions which are non-fluorescent and are not attacked by oxygen, iodine, or bromine in the cold, is easily reduced to anthranol by zinc dust and acetic acid (anthraquinol is not reduced), and is unchanged by cold aqueous alkalis. Boiling alkalis convert oxanthrone into anthraquinol. The two substances can be fused without changing the one into the other. Also, in boiling solvents they are for the most part unchanged; the addition of a catalyst, however, such as hydrogen chloride or sodium acetate, to the alcoholic solutions causes an almost complete change of the oxanthrone into anthraquinol. *Oxanthrone acetate*, $C_6H_4<\overset{CO}{\underset{CH(OAc)}{}}>C_6H_4$, m. p. 108°, is obtained from bromoanthrone and potassium acetate in hot glacial acetic acid; the action of acetyl chloride on oxanthrone in pyridine yields Liebermann's anthraquinyl diacetate.

Meisenheimer's methoxyanthrone, $C_6H_4<\overset{CO}{\underset{CH(OMe)}{}}>C_6H_4$, obtained by boiling bromoanthrone with methyl alcohol, is partly converted by boiling alcohol and hydrochloric acid or by luke-warm dilute sodium hydroxide into *anthraquinyl methyl ether*,

$$C_6H_4<\overset{C(OH)}{\underset{C(OMe)}{}}>C_6H_4,$$

m. p. 164°, which is also obtained by shaking an alkaline solution of anthraquinol with methyl sulphate, filtering in hydrogen, and extracting the filtrate with ether in an atmosphere of carbon dioxide. The ether forms an *acetate*, m. p. 174°, and a *benzoate*, m. p. 224°, separates in stout, brown crystals, yields solutions with a bluish-green fluorescence, and dissolves in cold alkalis, forming reddish-yellow solutions which are easily oxidised by iodine, bromine, or oxygen to anthraquinone and 9 : 9'-*dimethoxydianthrone*,

$$CO<\overset{C_6H_4}{\underset{C_6H_4}{}}>C(OMe)\cdot C(OMe)<\overset{C_6H_4}{\underset{C_6H_4}{}}>CO,$$

m. p. 239–240°. *Anthraquinyl dimethyl ether*,

$$C_6H_4<\overset{C(OMe)}{\underset{C(OMe)}{}}>C_6H_4,$$

m. p. 202°, obtained as a by-product in the reaction between anthraquinol and methyl sulphate, forms colourless plates with a blue fluorescence; its solutions also are fluorescent, and are not attacked by iodine or bromine in the cold. *Anthraquinyl diethyl ether*, m. p. 148°, obtained from anthraquinol and ethyl sulphate and purified by means of 80% alcohol, forms colourless needles with a blue fluorescence; its solution in chloroform or carbon disulphide is decolorised by bromine, anthraquinone being formed. The alcoholic mother-liquor contains Liebermann's ethyloxanthrone, m. p. 107°.

By a consideration of the distribution of the residual affinity, Meisenheimer has shown that addition takes place at the *meso*-carbon

atoms in derivatives of anthracene, and at the oxygen atom in those of anthrone and anthraquinone. The author shows that this theory is applicable, not only to explain, but also to predict, the preceding results. C. S.

Anthracene. II. Oxidation of Anthracene. KURT H. MEYER (*Annalen*, 1911, **379**, 73—78. Compare preceding abstract).—Most oxidising agents which attack anthracene convert it into anthraquinone. By using lead dioxide and glacial acetic acid, Schulze obtained a substance which was supposed to be different from anthraquinol (oxanthranol), and was called *β*-oxanthranol. It is, however, anthraquinol itself, produced, as the sequel shows, from the initially-formed oxanthrone acetate by the boiling alkali used by Schulze in the process of purification.

By oxidising anthracene in glacial acetic acid at 50° by lead dioxide (1 mol.), the author obtains 40—50% of anthranyl acetate, together with a little oxanthrone acetate and anthraquinone. When the oxidation is effected at 70° by 2 mols. of lead dioxide, the main product is oxanthrone acetate.

The oxidation of anthracene by manganese dioxide, cerium acetate, or vanadic acid proceeds in a similar manner, provided that glacial acetic acid is used as the solvent; a solution of anthracene in alcohol and toluene is oxidised by manganese dioxide and a drop of sulphuric acid to viscous products, amongst which occurs dianthrone.

Anthracene is oxidised very smoothly to oxanthrone by bromine in aqueous acetone, only a trace of anthraquinone being formed; the action of chlorine on an aqueous suspension of anthracene is similar, but less satisfactory, as regards purity of product. By allowing solutions of anthracene in glacial acetic acid and of bromine in methyl alcohol to flow simultaneously into a large volume of methyl alcohol, methoxyanthrone together with a little anthraquinone and unchanged anthracene are produced. C. S.

***p*-Xylyl Sulphide and its Derivatives.** Z. MARTYNOWICZ (*Chem. Zentr.*, 1910, ii, 1048; from *Kosmos*, 1910, **35**, *Radziszewski-Festband*, 594—596).—p-*Xylyl sulphide*, $S(CH_2 \cdot C_6H_4Me)_2$, obtained by the action of an alcoholic solution of potassium sulphide on *p*-xylyl bromide, forms colourless needles, m. p. 76°. By oxidation with nitric acid, it forms p-*xylylsulphoxide*, $SO(CH_2 \cdot C_6H_4Me)_2$, which crystallises in silky needles, m. p. 117°. Both these substances form on oxidation with potassium permanganate, p-*xylylsulphone*, $SO_2(CH_2 \cdot C_6H_4Me)_2$, which forms shining plates, m. p. 197°. N. C.

The Action of Ammonia on Aromatic Thiocyanates. MARYA STRZELECKA (*Chem. Zentr.*, 1910, ii, 1135; from *Kosmos*, 1910, 35, *Radziszewski-Festband*, 585—589).—When aromatic thiocyanates are boiled for a long time with alcoholic ammonia, ammonium cyanide is split off with the formation of disulphides. In this way the following disulphides were prepared: benzyl disulphide, $(CH_2Ph)_2$, white crystals, m. p. 71—72°; p-*xylyl disulphide*, white radiating tufts of needles, m. p. 43°; o-*xylyl disulphide*, white plates, m. p. 83—85°. The *meta*-compound could not be obtained in this way. N. C.

Phenyl **Thiocarbonate.** ANGELO CASOLARI (*Gazzetta*, 1910, 40, 389—402).—Potassium trithiocarbonate reacts with diazobenzene loride in aqueous solution with formation of *phenyl trithiocarbonate*, S_3Ph_2, which is a red oil, D_4^3 1·2668, $D_4^{19\cdot5}$ 1·2497. It has the normal olecular weight. Heat decomposes the substance somewhat readily, ith formation of hydrogen sulphide and carbon disulphide among her products. When subjected to distillation, the compound evolves apour at 210—215°/30 mm., and the distillate consists of phenyl sulphide. The action of alcoholic potassium hydroxide, alcoholic mmonia, or aqueous ammonia in a sealed tube, leads to the oduction of thiophenol, carbon disulphide, a carbonate, and a thio-lphate. As secondary products from the carbon disulphide are rmed thiocyanic acid and hydrogen sulphide (when ammonia is ed) and xanthic acid (with alcoholic potassium hydroxide).

Thiosulphates give a characteristic blue coloration when treated th a few drops of a 5% solution of sodium nitroprusside which has en exposed to light and air until it has assumed a chestnut-brown lour. The coloration is green in very dilute solutions; it is stable neutral solutions or in the presence of potassium hydrogen tartrate, t becomes green and finally yellow in the presence of alkali, acid, or idisers. The reaction is not given by sulphites or by tetrathionates. ie reagent may also be made by treating a fresh solution of sodium troprusside with potassium ferricyanide, then with potassium droxide, and finally rendering the liquid just acid with potassium drogen tartrate. R. V. S.

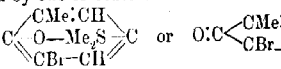
Sulphur Derivatives of *o*-**Cresol.** THEODOR ZINCKE and R. IUNE (*Ber.*, 1911, **44**, 185—197. Compare Zincke and Glahn, bstr., 1907, i, 698).—*3-Bromo-o-cresol-5-sulphonyl chloride*, $OH\cdot C_6H_2BrMe\cdot SO_2Cl$, epared by the action of phosphoryl chloride on potassium bromo-resol-sulphonate (Claus and Jackson, Abstr., 1889, 129) at 150°, ystallises from light petroleum in colourless needles, m. p. 94°, and elds an *acetyl* derivative in the form of colourless prisms, m. p. 131°. ie *methyl* ester, $OH\cdot C_6H_2MeBr\cdot SO_2Me$, forms colourless plates, m. p. 1—142°; the *ethyl* ester, compact needles, m. p. 113°, and the *ilide*, minute crystals, m. p. 165—166°. Potassium acetate reacts th an acetone solution of the chloride, yielding a polymeric *omosulphonyl-p-toluquinone*, $\left[SO_2{:}C\!<\!\begin{matrix}CH{:}CMe\\CH{=}CBr\end{matrix}\!>\!C{:}O\right]_n$, which crys-llises from nitrobenzene in small, colourless needles, with no definite p. *3-Bromo-5-thiol-o-cresol*, $SH\cdot C_6H_2MeBr\cdot OH$, obtained by lucing the sulphonyl chloride with zinc dust, alcohol, and hydro-loric acid, crystallises from light petroleum in colourless needles, p. 51—52°. The *diacetyl* derivative, $C_{11}H_{11}O_3SBr$, forms small, mpact plates, m. p. 111—112°. Concentrated ferric chloride ution oxidises the thiol in the presence of glacial acetic acid to *romo-o-cresol 5-disulphide*, $S_2(C_6H_2BrMe\cdot OH)_2$, which crystallises m light petroleum in thick, yellow plates, m. p. 123—124°. The responding *acetyl* derivative, $C_{18}H_{16}O_4S_2Br_2$, forms colourless plates,

m. p. 101—102°, and is also formed when the thiol is warmed with acetic anhydride and a little sulphuric acid.

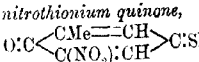
3-Bromo-5-methylthiol-o-cresol, $OH\cdot C_6H_2MeBr\cdot SMe$, obtained by methylating the thiol with methyl iodide and sodium methoxide in the cold, is a colourless oil, b. p. 167—169°/20—21 mm., and yields an *acetyl* derivative, $C_{10}H_{11}O_2SBr$, in the form of glistening, rhombic plates, m. p. 53°. When shaken with water the methyl sulphide yields a yellow, amorphous powder, $C_{33}H_{33}O_4S_4Br$, m. p. about 90° after sintering at 50—60°. Dilute alkali hydroxide solutions react in much the same manner as water. Sodium nitrite reacts with a glacial acetic acid solution of the methyl sulphide, yielding *3-nitro-5-methylthiol-o-cresol*, $SMe\cdot C_6H_2Me(NO_2)\cdot OH$, which crystallises in orange-red needles, m. p. 78—79°; its *acetyl* derivative forms yellow needles, m. p. 70°. *3-Bromo-o-cresol 5-methylsulphoxide*, $OH\cdot C_6H_2MeBr\cdot SOMe$, obtained by oxidising a glacial acetic acid solution of the methyl sulphide with hydrogen peroxide, crystallises from benzene in well-developed, colourless needles, m. p. 121°; it dissolves in alkalis without decomposition, and yields a perbromide. The corresponding *sulphone*, $OH\cdot C_6H_2MeBr\cdot SO_2Me$, obtained by using excess of hydrogen peroxide, crystallises in colourless needles or prisms, m. p. 168°. *3:6-Dibromo-5-methylthiol-o-cresol perbromide*, $OH\cdot C_6HMeBr_2\cdot SMeBr_2$, exists in two modifications, namely, orange-red plates from acetic acid and brownish-violet needles from chloroform. Both forms lose bromine, yielding *3:6-dibromo-5-methylthiol-o-cresol*, $C_8H_8OSBr_2$, which crystallises from light petroleum in colourless needles or rhombic plates, m. p. 111—112°. *3:6-Dibromo-o-cresol 5-methylsulphoxide*, $OH\cdot C_6HMeBr_2\cdot SMeO$, prepared by the action of water on the perbromide, crystallises from benzene in stout, colourless needles, m. p. 168°, and the corresponding *sulphone*, $C_8H_8O_2SBr_2$, forms colourless needles, m. p. 169°.

3-Bromo-o-cresol-5-dimethylsulphinium iodide, $OH\cdot C_6H_2MeBr\cdot SMe_2I$, prepared by the action of methyl iodide on the thiol derivative in the presence of an excess of alkali, crystallises in felted needles, m. p. 114° (decomp.). The corresponding *chloride*, $C_9H_{12}OSClBr$, forms slender needles, m. p. 151° (decomp.), and the *platinichloride* crystallises in brownish-yellow needles.

The *anhydro*-compound, $C_9H_{11}OSBr$, obtained by the action of moist silver oxide on the sulphinium iodide, crystallises in colourless needles, m. p. 185—187°, after darkening at 170°. It must be represented by one or other of the formulæ:



The corresponding *nitrothionium quinone*,



crystallises in glistening, yellow needles, m. p. 245—246°, and when boiled for some time with dilute alkalis yields the nitromethylthiolcresol. The *nitrate*, $C_9H_{11}O_3NS,HNO_3$, forms stout, yellow prisms, m. p. 150—151° (decomp.); the *chloride* forms pale yellow plates, m. p. 99—100° (decomp.), and the *platinichloride*, $2C_9H_{11}O_3NS,H_2PtCl_6$, forms compact, yellow needles.

J. J. S.

Action of Magnesium Phenyl Bromide on Heptaldehyde. V. Colacicchi (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 600—605).—*Phenylhexylcarbinol*, $C_{13}H_{20}O$ (from magnesium phenyl bromide and heptaldehyde), is a colourless liquid, b. p. 156°/25 mm., 176°/40 mm., or 275° at the ordinary pressure, D 0·9455, *n* (yellow) 1·501. Its *phenylurethane*, $C_{20}H_{25}O_2N$, forms rosettes of colourless crystals, m. p. 77°. The *phenylthiourethane* crystallises in laminæ, m. p. 147°. Phenylhexylcarbinol, when reduced with iodine and phosphorus, yields the corresponding *iodide*, which is a liquid, b. p. 140°/38 mm., and a *substance* (probably a hydrocarbon) distilling at 290—360°. By oxidation of the carbinol, phenyl hexyl ketone is obtained, identical with that described by Auger (Abstr., 1887, 814). The *semicarbazone* of the ketone, $C_{14}H_{21}ON_3$, forms colourless needles, m. p. 118—119°. The *p-nitrophenylhydrazone*, $C_{19}H_{23}O_2N_3$, crystallises in yellow needles, m. p. 127—128°.

Experiments on the physiological action of the compounds described show that the toxicity of the alcohol is somewhat greater than that of the ketone, both for warm-blooded (*Mus musculus*) and cold-blooded (*Rana esculenta*) animals. Both substances eventually cause paralysis of the central nervous system, and diminish the amplitude of the beats of the heart, which finally stops in diastole. R. V. S.

Dextrorotatory Phytosterols of Anthemis nobilis (Anthesterols). Timothée Klobb (*Compt. rend.*, 1911, **152**, 327—330. Compare Abstr., 1909, i, 471).—The existence of isomeric benzoates and the variable composition of its bromo-derivatives suggest that anthesterol is not a single substance. To throw light on this point, the alcohol was treated with acetic anhydride, when three isomeric acetates were obtained. A. Hexagonal lamellæ, m. p. 245—248°, $[\alpha]_D$ +91·2°; this yields *α*-anthesterol on hydrolysis. B. Hexagonal lamellæ, m. p. 225—230°, $[\alpha]_D$ +73·9°; *β*-anthesterol is obtained on hydrolysis. (C) Confused crystals, m. p. 185—195°, giving on hydrolysis needles having a double m. p., 158—160° and 185—190°.

On bromination the acetate, (A) yields two *monobromo*-derivatives, $C_{31}H_{50}OBrAc$, m. p. about 180°, but having $[\alpha]_D$ +133° and +58·8° respectively. (B) gives a *dibromo*-additive product, $C_{31}H_{51}OBr_2Ac$, m. p. 170—175°. (C) forms a mixture of the bromo-acetate from (A), with a substance corresponding in composition with a mixture of the (A) and (B) bromo-derivatives containing 45% of the latter.

The interpretation placed on these results is that anthesterol has the formula $C_{31}H_{52}O,3H_2O$, and is an individual substance homologous with amyrin and paltreubin (Jungfleisch and Leroux, Abstr., 1906, i, 525; 1907, i, 783; 1908, i, 1000). It is not identical with lupeol as suggested by Cohen (Abstr., 1908, i, 882). W. O. W.

Esterification of Benzamide and the Preparation of *N*-Substituted Benzamides. E. Emmet Reid (*Amer. Chem. J.*, 1911, **45**, 38—47).—Bonz (Abstr., 1889, 335) made a study of the reversible reaction: $CH_3{\cdot}CO{\cdot}NH_2 + EtOH \rightleftarrows CH_3{\cdot}CO_2Et + NH_3$, and identified ethylamine among the reaction products. He assumed that the amine was produced by the action of ammonia on the ester previously formed,

thus: $CH_3 \cdot CO_2Et + NH_3 = CH_3 \cdot CO_2 \cdot NH_3Et$, but his results are more simply accounted for by supposing that the amide and alcohol react directly to form acetoethylamide:

$$CH_3 \cdot CO \cdot NH_2 + EtOH = CH_3 \cdot CO \cdot NHEt + H_2O.$$

In connexion with certain other work (Abstr., 1910, i, 481, 701), the author studied the action of alcohol on benzamide and found that benzoethylamide could be readily obtained. The work has been continued and extended to other alcohols. The reactions which take place when ethyl alcohol is heated with benzamide are as follows: $C_6H_5 \cdot CO \cdot NH_2 + EtOH \rightleftarrows C_6H_5 \cdot CO_2Et + NH_3$, $C_6H_5 \cdot CO \cdot NH_2 + EtOH = C_6H_5 \cdot CO \cdot NHEt + H_2O$. The benzoethylamide undergoes hydrolysis according to the reaction:

$$C_6H_5 \cdot CO \cdot NHEt + H_2O \rightleftarrows C_6H_5 \cdot CO_2H, NH_2Et,$$

which finally reaches equilibrium.

Benzamide was heated with a slight excess of the alcohol in a sealed tube at 220—230° for periods varying from two to seven days. In an experiment with methyl alcohol, 39% of benzomethylamide was isolated, but no methyl benzoate was obtained, and 61% of the amide underwent hydrolysis. In two experiments with ethyl alcohol, the yields of benzoethylamide were 61·1 and 62·6%, of ethyl benzoate 1·27 and 1·58%, whilst the amounts of amide hydrolysed were 38·1 and 36·4%. With propyl alcohol the yield of benzopropylamide was 72·9%, of propyl benzoate 5·2%, and the amide hydrolysed amounted to 23·1%. In the case of *iso*butyl alcohol, 69·4% of benzo*iso*butylamide was obtained and 8·3% of *iso*butyl benzoate, whilst 24·3% of the amide suffered hydrolysis.

The amount of benzamide transformed into the ester seems to increase with the molecular weight of the alcohol. In the case of the experiment with methyl alcohol, a small quantity of water was present, and a large amount of hydrolysis therefore occurred.

The action of alcohols on benzamide affords a convenient method for preparing certain benzoalkylamides, and may also be of service for the preparation of the amines which are obtained as by-products.

E. G.

Study of *o*-Amino-*p*-sulphobenzoic Acid with Special Reference to its Fluorescence. Joseph H. Kastle (*Amer. Chem. J.*, 1911, **45**, 58—78).—Aqueous solutions of *p*-aminobenzoic sulphimide exhibit a bluish-purple fluorescence, but solutions in concentrated hydrochloric acid are not fluorescent. Since several difficulties arise in attempting to elucidate the causes of this phenomenon, the author has studied *o*-amino-*p*-sulphobenzoic acid (Hart, Abstr., 1881, 1146), which, on account of its simpler constitution, appeared more suitable for an investigation of the influence of simple chemical changes on fluorescence.

o-Amino-*p*-sulphobenzoic acid crystallises with $\frac{1}{2}H_2O$, and in dilute aqueous solution exhibits a bluish-purple fluorescence which, within certain wide limits, is inversely proportional to the concentration. The intensity of the fluorescence of both the acid and its salts is diminished by heat. The fluorescence of aqueous solutions of the acid is weakened or destroyed by strong acids and alkalis, the power of

effecting this change being roughly proportional to the degree of ionisation of the reagent. The intensity of the fluorescence of sodium, potassium, ammonium, calcium, barium, and magnesium *o*-amino-*p*-sulphobenzoates is independent of the nature of the base. Solutions of the acid and of the acid salts are much more fluorescent than those of the normal salts, whilst the fluorescence of solutions of the acid salts is somewhat more intense than that of solutions of the free acid.

Di-silver o-amino-p-sulphobenzoate exists in two forms, one amorphous and unstable above 27·5°, the other crystalline, stable at 27·5° and at higher temperatures, and less soluble in water than the amorphous variety. By the action of ethyl iodide on the crystalline di-silver salt, a compound, probably *o-ethylamino-p-sulphobenzoic acid*, $CO_2H\cdot C_6H_3(NHEt)\cdot SO_3H,H_2O$, m. p. 243° (decomp.), is produced, which forms colourless, rhombic crystals, and exhibits a blue fluorescence in dilute aqueous solution. In one experiment, another *compound*, m. p. 160°, probably either the true diethyl ester or the acid ester of the ethylamino-acid, $CO_2Et\cdot C_6H_3(NHEt)\cdot SO_3H$, was obtained, which forms pale yellow crystals, and, when boiled with water, is converted into the substance melting at 243°. A *barium* salt, probably $[CO_2Et\cdot C_6H_3(NHEt)\cdot SO_3]_2Ba$, has also been prepared.

E. G.

Iminosulphides. I. The Condensation of Thiobenzamide with Benzonitrile. Motooki Matsui (*Mem. Coll. Sci. Eng. Kyoto*, 1910, **2**, 401—404).—Under the influence of hydrochloric acid, thiamides combine with nitriles to form iminosulphides of the constitution: $S(CR:NH)_2$.

Benziminosulphide, $S(CPh:NH)_2$, obtained in the form of its hydrochloride by the action of hydrochloric acid on an ethereal solution of thiobenzamide and benzonitrile, crystallises in light red needles, m. p. 71°; the *acetyl* derivative crystallises in orange needles. The *hydrochloride*, $C_{14}H_{12}NS,2HCl$, forms orange needles, m. p. 110—111°, and is decomposed by water, yielding the free base. The *picrate*, $C_{14}H_{12}NS,C_6H_3O_7N$, crystallises in light red, prismatic plates, containing one molecule of alcohol; when heated at 80°, the alcohol of crystallisation is lost, and the picrate is obtained as an amorphous, yellow substance, m. p. 114°.

F. B.

Degradation of Amino-acids by Fermentation with Yeast. Otto Neubauer and Konrad Fromherz (*Zeitsch. physiol. Chem.*, 1911, 70, 326—350. Compare Abstr., 1909, ii, 750).—Stress is laid on the possible analogy between the conversion of an amino-acid into alcohol by means of yeast and into fatty-acid in the mammalian organism. In each case it is considered that the ketonic acid $R\cdot CO\cdot CO_2H$ is the intermediate product.

It is shown that by the action of yeast on *a*-aminophenylacetic acid, benzoyl alcohol, phenylglyoxylic acid, *l*-mandelic acid, and *l*-acetyl aminophenylacetic acid are formed. Yeast is able to effect a partial reduction of phenylglyoxylic acid to *l*-mandelic acid. The ketonic acid, *p*-hydroxylphenylpyruvic acid, is converted by yeast to a large extent

into *p*-hydroxyphenylethyl alcohol. *p*-Hydroxyphenyl-α-lactic acid, on the other hand, is not converted to any extent into *p*-hydroxyphenylethyl alcohol, proving that this alcohol acid is not the intermediate product between keto-acid and alcohol. The conversion of amino-acid into alcohol involves a series of alternate oxidative and reducing changes.

E. F. A.

Transformation of δ-Phenyl-Δ^{α}-pentenoic Acid into the Δ^{γ}-Isomeride. J. Bougault (*Compt. rend.*, 1911, 152, 196—197).—Fittig (Abstr., 1895, ii, 204) has shown that β-hydroxyvaleric acid is formed on boiling δ-phenyl-Δ^{α}-pentenoic acid with aqueous alkalis, together with a substance which he supposed to be δ-phenyl-Δ^{β}-pentenoic acid. The present author has been unable to obtain the latter substance, but finds that the Δ^{γ}-acid is an important product of the transformation, under the most favourable conditions the yield amounting to 50%. The formation of β-hydroxyvaleric acid was confirmed. An acidic liquid, possibly a mixture, is also produced in small quantity.

W. O. W.

Introduction of the Carboxylic Group into Polynuclear Aromatic Hydrocarbons. Carl Liebermann and M. Zsuffa (*Ber.*, 1911, 44, 202—210).—The methods of Graebe and Liebermann (*Ber.*, 1869, 2, 678), Friedel and Crafts (this Journ., 1877, ii, 725), and Gattermann (Abstr., 1888, 574) for the introduction of the carboxylic group into polynuclear aromatic hydrocarbons give but poor yields, and in many cases do not work. The authors have prepared the following acids by treating the corresponding hydrocarbons with 2·5 times their weight of oxalyl chloride at 160—170°, and extracting with cold sodium carbonate solution; the numbers indicate the percentage yields: anthracene-9-carboxylic acid, m. p. 217° (70—80%); fluorenecarboxylic acid (this Journ., 1877, ii, 493) (7—10%); indenecarboxylic acid, by using a temperature of 140—145° (15%), m. p. 234° (compare Perkin and Révay, Trans., 1893, 65, 238); acenaphthenecarboxylic acid, also obtained by heating at 180° for fourteen hours (30%) (compare Gattermann, Abstr., 1888, 574); phenanthrene-9-carboxylic acid (yield poor); chrysenecarboxylic acid, by heating for two days at 170°, yield poor.

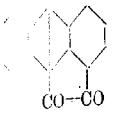
Better yields are obtained when aluminium chloride is added to the hydrocarbon and oxalyl chloride. The mixture becomes quite black even when carbon disulphide is present, but on adding water, the colour changes to yellow or red. The yields are better, but the products less pure.

Naphthalene gives a mixture of 80% of α- and β-naphthoic acids, and anthracene yields anthracene-9-carboxylic acid (30%) and aceanthrenequinone (60%).

Benzene and naphthalene are not carboxylated in the absence of aluminium chloride, and when anthracene is heated with excess of oxalyl chloride at 200°, 10-chloroanthracene-9-carboxylic acid is formed (70%) (compare Behla, Abstr., 1886, 248; 1887, 593).

Chrysenecarboxylic acid, $C_{18}H_{11}\cdot CO_2H$, crystallises from alcohol in colourless needles, m. p. 303°, and the *sodium* salt, $C_{19}H_{11}O_2Na$, crystallises from water in long plates.

Acenanthrenequinone (annexed formula) crystallises from benzene in brilliant red prisms, m. p. 270°, and when sublimed has the appearance of alizarin. It combines with sodium hydrogen sulphite, is oxidised by chromic acid to anthraquinonecarboxylic acid, and an acetic acid solution reacts with an alcoholic solution of *o*-toluylenediamine, yielding *aceanthrenetolazin*,



$$C_{14}H_8\langle\begin{matrix}C{:}N\\ |\\ C{:}N\end{matrix}\rangle C_6H_3Me.$$

This crystallises in orange-red needles or plates, m. p. 237°, and its alcoholic solution has a green fluorescence. J. J. S.

Preparation of 3:5-Di-iodotyrosine from Iodoprotein. Adolf Oswald (*Zeitsch. physiol. Chem.*, 1911, 70, 310—313).—3:5-Di-iodotyrosine has been isolated among the products of the hydrolysis of iodo-albacid with barium hydroxide (Blum and Vaubel, Abstr., 1898, i, 610). It is suggested that iodine is, in part, attached to tyrosine in the natural iodoproteins. E. F. A.

Conversion of Coumarins into Coumarinic Acids and o-Coumaric Acids. II. Karl Fries and W. Volk (*Annalen*, 1911, 379, 90—110. Compare Abstr., 1908, i, 820).—Experiments similar to those already recorded (*loc. cit.*) have been performed on 4-methylcoumarin, 3-methylcoumarin, and 3-ethylcoumarin.

The conversion of 4-methylcoumarin into β-methylcoumarinates by aqueous alkalis is slower than that of coumarin into a coumarinate, but, conversely, its conversion by concentrated alkali into *β-methyl-o-coumaric acid*, $OH\cdot C_6H_4\cdot CMe{:}CH\cdot CO_2H$, m. p. 154° (decomp.), proceeds more readily (five hours' boiling with 33% potassium hydroxide) than that of coumarin into *o*-coumaric acid. When 4-methylcoumarin is heated with alcoholic potassium ethoxide at 140—150° for fifteen hours and the product is acidified, *1-(2-methylcoumaran)-3-(4-methylcoumarin) ketone* (3-[*2-methylhydrocoumarilyl*]-*4-methylcoumarin*), $C_{20}H_{16}O_4$, m. p. 224°, is obtained, the constitution and behaviour of which are similar to those of the ketone obtained in the same manner from 4:7-dimethylcoumarin (*loc. cit.*); when boiled for a short time with dilute aqueous alkali, it loses carbon dioxide and yields *di-1-(2-methylcoumaran) ketone* (1-[*2-methylhydrocoumarilyl*]-*2-methylhydrocoumarone*), $\left(C_6H_4\langle\begin{matrix}CHMe\\ |\\ O\end{matrix}\rangle CH\right)_2CO$, m. p. 183—185°, solidifying to a glassy mass which has m. p. about 95°, resolidifies at about 145°, and melts again at 184°. This substance forms yellow solutions in alkalis, and yields an *oxime*, m. p. 213°.

3-Methyl-(or ethyl-)coumarin behaves towards aqueous alkalis and sodium ethoxide like those coumarins which are not alkylated in the pyrone nucleus. After being boiled for five hours with 33% potassium hydroxide, only salts of the alkylcoumarinic acid are formed, since carbon dioxide causes the precipitation of the 3-alkylcoumarin. When boiled for five hours with alcoholic sodium ethoxide, however, the 3-alkylcoumarins yield salts of the *α*-alkyl-*o*-coumaric acids, although more slowly than is the case with coumarin and its *Bz*-homologues.

α-*Methyl-o-coumaric acid*, $OH\cdot C_6H_4\cdot CH:CMe\cdot CO_2H$, m. p. 135° (decomp.), and α-*ethyl-o-coumaric acid*, m. p. 181° (decomp.), form yellow solutions in concentrated sulphuric acid, yield alkali salts which exhibit a yellowish-green fluorescence in solution (the alkali salts of β-alkyl-o-coumaric acids do not show fluorescence), and are not reconverted into the 3-alkylcoumarins very smoothly, in this respect resembling *o*-coumaric acid, but differing from β-alkyl-*o*-coumaric acids.

The replacement by methyl groups of hydrogen atoms in the benzene nucleus of coumarins does not affect greatly the behaviour of the resulting alkylcoumarins, except in so far as slight variations in the velocity of formation of the *o*-coumaric acids are concerned. It is very striking, therefore, that the introduction of hydroxy-, methoxy-, or dimethylamino-groups in the *Bz*-nucleus prevents completely the formation of the corresponding *o*-coumaric acids; thus 4-methylumbelliferone, its methyl ether, and 7-dimethylamino-4-methylcoumarin are only converted into the corresponding coumarinates even after prolonged boiling with alcoholic sodium ethoxide or concentrated aqueous potassium hydroxide. 7-Dimethylamino-4-methylcoumarin is decomposed completely by boiling for six hours with 40% potassium hydroxide, *m*-dimethylaminophenol being formed.

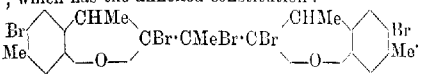
7-*Methylcoumarin-4-acetic acid*, $C_6H_3Me<\begin{matrix}C(CH_2\cdot CO_2H)\\ -O\cdot CO-\end{matrix}>CH$, m. p. 190° (decomp.; thereby yielding 4:7-dimethylcoumarin), obtained together with its ethyl and *m*-tolyl esters by the interaction of *m*-cresol, ethyl acetonedicarboxylate, and concentrated sulphuric acid at 0°, does not behave like 4-methylcoumarin; with aqueous alkalis it does not form an *o*-coumarate, and with alcoholic sodium ethoxide a ketone is not produced, in both cases a coumarinate being formed which is easily reconverted into the coumarin by acids. The *ethyl* ester, $C_{14}H_{14}O_4$, m. p. 132°, behaves in a similar manner, being hydrolysed by aqueous alkalis and yielding a coumarinate with sodium ethoxide. The m-*tolyl* ester, $C_{19}H_{16}O_4$, m. p. 214°, however, behaves differently. By prolonged boiling with 20% potassium hydroxide, it is partly hydrolysed, partly unchanged, and partly converted into the following *o*-coumaric acid and a substance which yields 2:2:4:6-tetrabromo-3-keto-2:3-dihydrotoluene (Foster, Dissert., Marburg, 1898) by treatment with bromine. By treatment with alcoholic potassium ethoxide at 130—140° for fifteen hours, the *m*-tolyl ester yields, after acidifying the product, the m-*tolyl* ester of α-*acetic-4-methyl-o-coumaric acid*,

$$OH\cdot C_6H_3Me\cdot C(CH_2\cdot CO_2\cdot C_6H_4Me):CH\cdot CO_2H,$$

which sinters at 95°, melts and decomposes at about 100°, resolidifies at about 120°, and melts again at 214°, the m. p. of the corresponding coumarin. The acid is remarkably unstable, being converted into the coumarin by acids or organic solvents.

The following two ketones obtained from 4:6-dimethylcoumarin correspond in constitution with those prepared from 4:7-dimethylcoumarin (*loc. cit.*). By treatment with alcoholic potassium ethoxide at 160° for twenty-four hours and acidification of the product, 4:6-dimethylcoumarin yields 1-(2:4-*dimethylcoumaran*)-3-(4:6-*dimethyl*-

coumarin) *ketone* (3-[2 : 4-*dimethylhydrocoumarilyl*]-4 : 6-*dimethylcoumarin*), $C_{22}H_{20}O_4$, m. p. 275—280°, which is converted by boiling aqueous-alcoholic alkali into an intensely yellow solution, from which, by acidification, the ketone, $C_{21}H_{22}O_3$, m. p. 199°, already described (*loc. cit.*) is obtained. The ketone, $C_{21}H_{22}O_3$, is converted by ethereal magnesium methyl iodide in the usual way into the *compound*, $C_6H_3Me\langle{}^{CHMe}_{O}\rangle C{:}CMe{\cdot}CH\langle{}^{CHMe}_{O}\rangle C_6H_3Me$, m. p. 164°, which reacts with bromine in glacial acetic acid to form the *substance*, $C_6H_3Me\langle{}^{CHMe}_{O}\rangle CBr{\cdot}CMeBr{\cdot}CBr\langle{}^{CHMe}_{O}\rangle C_6H_3Me$, m. p. 200°. The corresponding compound, $C_{22}H_{24}O_2$, obtained from 4 : 7-dimethylcoumarin (*loc. cit.*), yields by bromination a *substance*, $C_{22}H_{21}O_2Br_3$, m. p. 225°, which has the annexed constitution :



C. S.

Method for the Preparation of Derivatives of α-Cyanoacrylic Acids. C. H. Clarke and Francis Francis (*Ber.*, 1911, 44, 273—276).—Instead of condensing aldehydes with cyanoacetic acid or its ester, the authors use substances which will form cyanoacetic acid, for example, potassium bromoacetate and potassium cyanide : $CH_2Br{\cdot}CO_2K + KCN + R{\cdot}CHO = R{\cdot}CH{:}C(CN){\cdot}CO_2K + KBr + H_2O$. The best yields are obtained when the potassium salt of the bromoacetic acid is added to an aqueous solution of the cyanide and aldehyde. Potassium cyanide accelerates the reaction between aromatic aldehydes and salts of cyanoacetic acid, just as sodium ethoxide does (Carrick, Abstr., 1890, 1270; 1892, 1086). The following compounds have been prepared by this method : α-cyanocinnamic acid, α-cyano-β-anisylacrylic acid, α-cyano-β-styrylacrylic acid, α-cyano-β-piperonylacrylic acid, and α-cyano-β-furfurylacrylic acid.

Ethyl α-cyano-β-piperonylacrylate, $C_{13}H_{11}O_4N$, crystallises from alcohol in colourless plates, m. p. 104°. *α-Cyanoferulic acid*, $OMe{\cdot}C_6H_3(OH){\cdot}CH{:}C(CN){\cdot}CO_2H$, prepared from vanillin, potassium bromoacetate, and potassium cyanide, crystallises from dilute alcohol in pale yellow needles, m. p. 215°. The corresponding *ethyl* ester, $C_{13}H_{13}O_4N$, has m. p. 111°.

α-Cyano-o-coumaric acid, $OH{\cdot}C_6H_4{\cdot}CH{:}C(CN){\cdot}CO_2H$, could not be obtained crystalline; its *benzoyl* derivative, $C_{17}H_{11}O_4N$, crystallises in needles, m. p. 210°. The acid is hydrolysed with great readiness to coumarinic acid. J. J. S.

Isomeric Phenylphthalimides and Some Allied Compounds. M. Mitsuru Kuhara and Shigeru Komatsu (*Mem. Coll. Sci. Eng. Kyōtō*, 1910, 2, 365—386).—By the action of acetyl chloride on phenylphthalamic acid, the authors (Abstr., 1909, i, 484) have previously obtained two isomeric phenylphthalimides. Of these two isomerides, the colourless form was represented by the formula :

$$C_6H_4\langle{}^{C(:NPh)}_{CO}\rangle O,$$

whilst the yellow variety was supposed to possess a peroxide structure.

The authors now consider that the colour of the yellow isomeride is due to the presence of the chromophoric group C:NPh, and have, therefore, assigned to this form the unsymmetrical formula given above. The constitution of the colourless isomeride remains undetermined.

Two isomeric substituted phenylphthalimides, colourless and yellow, are also produced by the action of phthalyl chloride on *o*-toluidine, *p*-toluidine, *m*-4-xylidine, *o*-3-xylidine, *p*-xylidine, and *ψ*-cumidine. The colourless isomerides possess the symmetrical constitution: $C_6H_4<^{CO}_{CO}>NAr$, whilst the coloured varieties are represented by the unsymmetrical formula: $C_6H_4<^{C(:NAr)}_{---CO---}>O$.

The colourless and yellow modifications of *p*-methoxyphenylphthalimide, *p*-ethoxyphenylphthalimide, and *p*-methoxyphenyl-Δ¹-dihydrophthalimide (Piutti and Abati, Abstr., 1903, i, 424) are considered by the authors to be structural isomerides, the yellow forms having an unsymmetrical, and the colourless varieties a symmetrical structure.

The formulæ assigned by Piutti (Abstr., 1908, i, 783) to the two modifications of *p*-hydroxyphenylmaleimide are to be interchanged.

The behaviour of the isomeric arylphthalimides towards alkylmagnesium halides has also been investigated, and it is found that both isomerides yield the same 3-hydroxy-2-aryl-3-alkylisoindolinone: $C_6H_4<^{---CO---}_{CR(OH)}>NAr$ (compare Sachs and Ludwig, Abstr., 1904, i, 266).

It is suggested that the latter compounds are formed from the *as*-arylphthalimides by a molecular arrangement according to the following scheme:

$$C_6H_4<^{---CO---}_{C(:NAr)}>O + RMgX + H_2O \longrightarrow \left[C_6H_4<^{CR(OH)}_{C(:NAr)}>O\right] \rightarrow C_6H_4<^{CR(OH)}_{CO}>NAr.$$

as-*o*-*Tolylphthalimide*, $CO<^{O}_{C_6H_4}>C{:}N\cdot C_6H_4Me$, obtained together with *s*-*o*-tolylphthalimide by the action of phthalyl chloride on *o*-toluidine in ethereal solution at −10°, crystallises in canary-yellow needles, m. p. 136—137°. On treatment with magnesium methyl iodide it yields 3-*hydroxy*-2-*o*-*tolyl*isoindolinone,

$$C_6H_4<^{CMe(OH)}_{CO}>N\cdot C_6H_4Me;$$

the latter forms colourless crystals, m. p. 161—162°, and is also produced by the action of magnesium methyl iodide on *o*-tolylphthalimide.

3-*Hydroxy*-2-*o*-*tolyl*-3-*ethyl*isoindolinone, $C_{17}H_{17}O_2N$, crystallises in colourless plates, m. p. 169—171°.

as-*p*-*Tolylphthalimide*, $C_{15}H_{11}O_2N$, crystallises in light yellow needles, m. p. 109—110°, and is formed simultaneously with *s*-*p*-tolylphthalimide by the action of phthalyl chloride on *p*-toluidine; with magnesium ethyl iodide, both these compounds yield 3-*hydroxy*-2-*p*-*tolyl*-3-

ethylisoindolinone, $C_{17}H_{17}O_2N$, which crystallises in colourless needles, m. p. 177—178°.

as-m-4-*Xylylphthalimide*, $CO<\begin{matrix}O\\C_6H_4\end{matrix}>C{:}N\cdot C_6H_3Me_2$, yellow needles, m. p. 142—143°, m-4-*xylylphthalamide*, $C_6H_4(CO\cdot NH\cdot C_6H_3Me_2)_2$, silky needles, m. p. 202—203°, and s-m-4-*xylylphthalimide*,

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\cdot C_6H_3Me_2,$$

slender needles, m. p. 154°, are produced by the interaction of phthalyl chloride and *m*-4-xylidine in ethereal solution. The first-named substance is converted by mineral acids or alkali into *s-m*-4-xylyl phthalimide, which is readily obtained by heating *m*-4-xylidine with phthalic anhydride or phthalyl chloride.

Di-m-4-*xylylphthaldi-imide*, $\begin{matrix}C_6H_4\cdot C{:}N\cdot C_6H_3Me_2\\CO\text{---}N\cdot C_6H_3Me_2\end{matrix}$, is produced, together with *s-m*-4-xylylphthalimide, by the interaction of phosphorus pentachloride and *m*-4-xylylphthalamide in chloroform solution; it forms yellow plates, m. p. 149—150°.

3-*Hydroxy*-2-m-4-*xylyl*-3-*ethylisoindolinone*,

$$C_6H_4<\begin{matrix}CEt(OH)\\CO\end{matrix}>N\cdot C_6H_3Me_2,$$

prepared from both *as-m*-4-xylylphthalimide and *s-m*-4-xylylphthalimide by the action of magnesium ethyl iodide, crystallises in colourless plates, m. p. 176—177°.

3-*Hydroxy*-2-m-4-*xylyl*-3-*methylisoindolinone*, $C_{17}H_{17}O_2N$, has m. p. 161—162°; from methyl- and ethyl-alcoholic solutions it crystallises with one molecule of alcohol.

o-3-*Xylylphthalamide*, $C_{24}H_{24}O_2N$, slender needles, m. p. 192—193°, is obtained by the interaction of *o*-3-xylidine and phthalyl chloride in ethereal solution; small quantities of a yellow substance, consisting probably of as-o-3-*xylylphthalimide*, $C_{16}H_{13}O_2N$, and of s-o-3-*xylylphthalimide*, $C_{16}H_{13}O_2N$, are produced simultaneously. The latter compound crystallises in colourless needles, m. p. 143—144°, and is readily obtained by heating *o*-3-xylidine with phthalic anhydride or phthalyl chloride.

Di-o-3-*xylylphthaldi-imide*, $C_{24}H_{22}ON_2$, prepared by the action of phosphorus pentachloride on *o*-3-xylylphthalamide, crystallises from alcohol in yellow plates, m. p. 123—124°.

p-*Xylylphthalamide*, $C_{24}H_{24}O_2N_2$, silky needles, m. p. 209—210°, s-p-*xylylphthalimide*, $C_{16}H_{13}O_2N$, slender needles, m. p. 147—148°, and as-p-*xylylphthalimide*, $C_{16}H_{13}O_2N$, amber-coloured needles, m. p. 178—181°, are obtained by the action of *p*-xylidine on phthalyl chloride in ethereal solution at a low temperature. The last-named substance is unstable, and readily changes into *s-p*-xylylphthalimide, which is more easily obtained by heating *p*-xylidine with phthalic anhydride.

Di-p-*xylylphthaldi-imide*, $C_{24}H_{22}ON_2$, obtained from *p*-xylylphthalamide and phosphorus pentachloride, crystallises in yellow plates, m. p. 133—134°.

ψ-Cumylphthalamide, $C_6H_4(CO\cdot NH\cdot C_6H_2Me_3)_2$, silky needles, m. p.

210—212°, and as-*ψ-cumylphthalimide*, $CO<\begin{matrix}-O-\\ C_6H_4\end{matrix}>C{:}N{\cdot}C_6H_2Me_3$, yellow needles, m. p. 117—118°, are obtained together with s-*ψ*-cumyl phthalimide by the interaction of *ψ*-cumidine and phthalyl chloride.

Di-ψ-cumylphthaldi-imide, $\begin{matrix}C_6H_4{\cdot}C{:}N{\cdot}C_6H_2Me_3\\ CO—N{\cdot}C_6H_2Me_3\end{matrix}$, is formed when *ψ*-cumylphthalamide is treated with phosphorus pentachloride in chloroform solution; it crystallises in yellow plates, m. p. 136—137°.

3-*Hydroxy*-2-*ψ-cumyl*-3-*ethylisoindolinone*,

$$C_6H_4<\begin{matrix}CEt(OH)\\ CO\end{matrix}>N{\cdot}C_6H_2Me_3,$$

colourless plates, m. p. 152—153°, is obtained by the action of magnesium ethyl iodide on both forms of *ψ*-cumylphthalimide.

F. B.

Spectrometric Examination of Guthzeit's *cyclo*Butane Derivatives. Erich Hartmann (*J. pr. Chem.*, 1911, [ii], 83, 190—194).—The stereoisomerides, $C_{30}H_{44}O_{16}$, m. p. 103° and 88° respectively (Guthzeit, Weiss, and Schäfer, Abstr., 1909, i, 933), and the ester, $C_{30}H_{42}O_{16}$, m. p. 86° (Guthzeit and Hartmann, Abstr., 1910, i, 386), have been examined by the spectrograph. The first two esters give almost identical absorption spectra in alcoholic solution; also in the presence of sodium ethoxide (2 mols.) they give spectra identical not only with each other, but also with that of ethyl sodiodicarboxyglutaconate; when the three solutions have been acidified, they show the spectrum of ethyl dicarboxyglutaconate. The ester, $C_{30}H_{42}O_{16}$, gives an absorption spectrum which is changed by the addition of sodium ethoxide (2 mols.), but is recovered by acidifying the alkaline alcoholic solution.

The results, which prove that the first two esters are depolymerised by the addition of sodium ethoxide, whilst the third merely forms a sodium derivative, are in complete harmony with the constitutions ascribed to the three substances (*loc. cit.*).

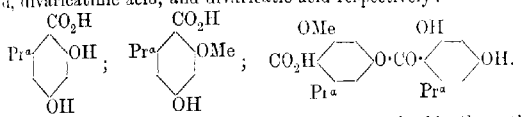
C. S.

Lichens, and their Characteristic Constituents. XII. Oswald Hesse (*J. pr. Chem.*, 1911, [ii], 83, 22—96).—A scientific classification of the lichens must be based on a chemical examination of their characteristic constituents. The present paper is very largely a repetition of the author's work in this region during the last fifty years. The new work deals mainly with the divergencies of the author's results from those of other observers.

Usnic acid is not a constant constituent of *Evernia prunasti*, as claimed by Zopf (*Flechtenstoffe*, 1907, 356), since the author failed to detect it in several samples of the lichen obtained from different localities. The same statement is true of *Evernia divaricata*.

A large quantity of *E. illyrica*, collected on the Trnovaner Walde, near Görz, has been worked up in the usual way, and the divaricatic acid isolated. It has not the formula $C_{22}H_{26}O_7$, as stated previously, but $C_{21}H_{24}O_7$, which is in agreement with Zopf's analyses. Its decomposition by concentrated hydriodic acid yields methyl iodide, carbon dioxide, and divarinol, not orcinol, as erroneously stated

elsewhere (*Biochemisches Handlexicon*, 7, 69). The *potassium*, *sodium*, *barium*, *calcium*, *copper*, and *silver* salts, the *methyl* and *ethyl* esters, and the *anhydride* are described. The acid, $C_{11}H_{14}O_4$, obtained by the author by boiling divaricatic acid with aqueous barium hydroxide (Abstr., 1898, i, 531), is identical with Zopf's divaricatinic acid, prepared by treating divaricatic acid with potassium hydroxide (Abstr., 1898, i, 489). The *barium* salt, *silver* salt, and *ethyl* ester, m. p. 41°, are described. By treating aqueous sodium divaricatate with an equivalent amount of aqueous ammonia, potassium hydroxide, or sodium hydroxide for forty-eight hours at the ordinary temperature, *divaric acid*, $C_{10}H_{12}O_4$, m. p. 169° (decomp.), is obtained, which in alcoholic solution reddens litmus and develops a purple-violet coloration with ferric chloride. It does not contain a methoxy-group, and is easily decomposed by boiling water, yielding carbon dioxide and divarinol. Pure hydrated divarinol, $C_9H_{12}O_2,H_2O$, has m. p. 44°, and loses its water completely in a desiccator at the ordinary temperature, forming a yellowish-red mass; its *diacetate* has m. p. 12—15°. Divarinol, which resembles orcinol in its behaviour, has the constitution $CH_3\cdot C<\begin{matrix}CH\cdot C(OH)\\ CH:C(OH)\end{matrix}>CH$; the annexed formulæ are those of divaric acid, divaricatinic acid, and divaricatic acid respectively:



Various samples of *E. furfuracea* have been examined by the author, and found to contain atranorin and evernuric acid, but not farinaceaic acid, as stated by Rave (*Dissert.*, 1908).

Evernia furfuracea, var. *olivetorina* (*Pseudevernia olivetorina*), contains atranorin and olivetoric acid, the *potassium*, *barium*, and *calcium* salts of which are described. The decomposition of olivetoric acid by boiling aqueous barium hydroxide in the absence of air yields carbon dioxide and a substance, *olivetorol*, $C_{20}H_{26}O_5$, which develops a purple-violet coloration with ferric chloride, and a blood-red coloration with calcium hypochlorite; its further examination has been postponed owing to lack of material.

Since Zopf found *l*-usnic acid, destrictic acid, and a colourless crystalline substance in *Cladonia destricta* (Abstr., 1903, i, 762), whilst the author isolated *l*-usnic acid, squamatic acid, cladestin, and some coloured substances (Abstr., 1905, i, 138), the lichen has been again examined, with the result that *l*-usnic acid, cladestin, squamatic acid, destrictic acid, and two new acids, *destrictasic acid* and *cladestic acid*, have been isolated. Destrictasic acid, $C_{15}H_{24}O_5$, m. p. 202°, sintering at 175°, forms white leaflets from dilute alcohol; its alcoholic solution reddens litmus, but does not develop colorations with ferric chloride or calcium hypochlorite.

The following new facts are stated with respect to cladestin: its m. p. is 242—245°, not 252°, it crystallises anhydrous, and it does not yield ethyl iodide by treatment with hydriodic acid, although it is so changed that its alcoholic solution no longer gives a coloration

with ferric chloride. Cladestic acid, $C_{50}H_{74}O_{12}$, is a flesh-coloured, amorphous powder, m. p. 82° (decomp.). It does not contain an alkyloxy-group, has a distinctly acid reaction in alcoholic solution, and develops an intense dark brown coloration with ferric chloride.

Cetraria stuppea contains dilichesteric acid, proto-α-lichesteric acid, and two new substances, called *cornicularin* and *stuppeaic acid*. Cornicularin, $C_{28}H_{44}O_5$, m. p. 230°, is crystalline, does not dissolve in potassium hydroxide or carbonate, and in alcoholic solution gives a dark brown coloration with ferric chloride. Stuppeaic acid, $C_{19}H_{32}O_4$, m. p. 222° (decomp.), is a crystalline powder, dissolves sparingly in the ordinary solvents, gives only a slight brown coloration with ferric chloride, and does not contain an alkyloxy-group. *Cetraria aculeata* contains, in addition to protolichesteric acid and proto-α-lichesteric acid, a new substance called *acanthellin*, $C_{18}H_{34}O_5$, m. p. 188°, which is apparently crystalline, sparingly soluble, and does not give a coloration with ferric chloride.

Stictaic acid, isolated from *Sticta pulmonaria*, probably has the composition $C_{19}H_{14}O_9$, rather than $C_{18}H_{14}O_9$, as stated previously. It is shown that conspersaic acid, isolated from *Parmelia conspersa*, is not identical with salazic acid, as suggested by Zopf (Abstr., 1905, i, 789).

Urceolaria albissima is stated by Zopf (Abstr., 1897, i, 430) to contain zeorin and atranorin, in addition to the lecanoric acid discovered by the author (Abstr., 1899, i, 381), but a repetition of his experiments on 400 grams of the lichen has failed to disclose the presence of these two substances; in one sample, however, atranorin has been discovered. Zopf has stated (Abstr., 1906, i, 672) that the lecanoric acid obtained by the author from *Urceolaria scruposa* (Abstr., 1901, i, 595) is diploschistessic acid; it is now shown that the latter is a mixture of lecanoric and patellaric acids. C. S.

o-Tolylacetaldehyde and its Derivatives. M. Kronik (*Chem. Zentr.*, 1910, ii, 1051; from *Kosmos*, 1910, 35, *Radziszewski-Festband*, 590—593).—*o-Tolylacetaldehyde*, $C_6H_4Me\cdot CH_2\cdot CHO$, is obtained by the dry distillation under reduced pressure of the barium salts of *o*-tolylacetic and formic acids; it forms an oily, yellow liquid, b. p. 219—221°/742 mm., b. p. 142—143°/90 mm., D_4^{15} 1·0241, and when diluted has an odour resembling that of jasmine. The *oxime* forms colourless needles, m. p. 99—100°. The *thiosemicarbazone* crystallises in rhombic plates. N. C.

The Carbonyl Group in the Nascent State. Alfred W. Stewart (*J. pr. Chem.*, 1911, [ii], 83, 194—197).—Reply to Petrenko-Kritschenko (Abstr., 1910, i, 177). C. S.

Halogenated Alicyclic Ketones. I. Monohalogenides of *cyclo*Hexanones. Arthur Kötz and H. Steinhorst (*Annalen*, 1911, 379, 1—27).—The paper deals with the conditions for the direct introduction of one chlorine or bromine atom into *cyclo*hexanone and its homologues, with the orientation of the halogen atom, and with the influence exerted by one or more alkyl groups in the cyclic ketone on

ie position of the halogen. It is found that the halogen always nters the ring in the ortho-position to the keto-group, and in the neta- or para-position to a methyl group, when such is present, except n the case of carvomenthone.

The halogenation of the cyclic ketones is effected by Kötz and Götz's process (Abstr., 1908, i, 173), by the action of chlorine, or of romine vapour mixed with air, in the presence of calcium carbonate and vater. The halogenated ketones are deprived of the elements of the ydrogen halogenide by ethereal aniline, and are converted by aqueous otassium carbonate into the corresponding hydroxy-compound, from hich the elements of water are removed by anhydrous oxalic acid at 10°; the same *cyclo*hexenone is always obtained by the two processes. Thus *cyclo*hexanone itself has already been shown to yield 2-chloro-(or romo-)*cyclo*hexanone (Kötz and Götz, *loc. cit.*). 1-Methyl*cyclo*hexan-3-one yields 3-*chloro*-1-*methyl*cyclo*hexan*-2-*one*,

$$CHMe\begin{<}CO\cdot CHCl\\CH_2\cdot CH_2\end{>}CH_2,$$

b. p. 98—100°/15 mm., and 3-*bromo*-1-*methyl*cyclo*hexanone*, b. p. 105—107°/12 mm.; the former is converted into 3-*hydroxy*-1-*methyl*-cyclo*hexan*-2-*one*, b. p. 85—87°/13 mm., from which, and also from the bromo-compound, 1-*methyl*-Δ^3-cyclo*hexen*-2-*one*, b. p. 172—173° (*semicarbazone*, m. p. 177—178°), is obtained. 1-Methyl*cyclo*hexan-3-one yields 4-*chloro*-1-*methyl*cyclo*hexan*-2-*one*, m. p. 61—62°, and 4-*bromo*-1-*methyl*cyclo*hexan*-3-*one*, m. p. 83—84°; 4-*hydroxy*-1-*methyl*cyclo*hexan*-3-*one* has b. p. 88—90°/14 mm., and 1-*methyl*-Δ^3-cyclo*hexen*-3-*one*, b. p. 188—190°, forms a *semicarbazone*, m. p. 159—160°. 1-Methyl*cyclo*hexan-4-one yields 3-*chloro*-1-*methyl*cyclo*hexan*-4-*one*, b. p. 99—101°/14 mm., from which 3-*hydroxy*-1-*methyl*cyclo*hexan*-4-*one*, b. p. 90—92°/14 mm., is obtained; the latter is oxidised to β-methyladipic acid, and yields with anhydrous oxalic acid, 1-*methyl*-Δ^3-cyclo*hexen*-4-*one*, b. p. 175—176° (*semicarbazone*, m. p. 184—185°), which is also obtained from 3-*bromo*-1-*methyl*cyclo*hexan*-4-*one*, b. p. 112—113°/14 mm.

Menthone yields 4-*bromomenthane*-3-*one*, b. p. 120—122°/16 mm., and 4-*chloromenthane*-3-*one*, b. p. 115—117°/15 mm., from which Wallach's Δ^4-menthene-3-one is obtained; an ethereal solution of the last yields with hydrogen chloride, 5-*chloromenthane*-3-*one*, m. p. 135—136°. Carvomenthone yields 1-*chloromenthone*-2-*one*, b. p. 130—132°/14 mm., and 1-*bromomenthane*-2-*one*, b. p. 128—130°/14 mm. The constitutions of the last two compounds are determined by their conversion into carvotanacetone. C. S.

Tetrahydroxybenzenes. Giuseppe Bargellini and Leda Bini (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 595—600).—The preparation is described of some derivatives of 1:2:3:5-tetrahydroxybenzene including 2:3:4:6-tetramethoxyacetophenone, the corresponding tetramethoxychalkone, and 4:2′:3′:4′:6′-pentamethoxychalkone.

When 1:2:3:5-tetramethoxybenzene is treated with acetyl chloride in presence of aluminium chloride in carbon disulphide solution, a mixture of the dimethyl (in small quantity), trimethyl, and tetramethyl ethers of 2:3:4:6-tetrahydroxyacetophenone is produced. The

first two are soluble in sodium hydroxide; they can be precipitated from it by addition of acid, and separated with the aid of solvents. 2:3:4:6-*Tetrahydroxyacetophenone dimethyl ether*, $C_{10}H_{12}O_5$, is a bright yellow, crystalline powder, m. p. 162—163°. It dissolves in concentrated sulphuric acid with production of an orange-yellow coloration, which on addition of nitric acid becomes intensely red. Its *acetyl* derivative has m. p. 110—112°. 2:3:4:6-*Tetrahydroxyacetophenone trimethyl ether*, $C_{11}H_{14}O_5$, forms slightly yellow, prismatic crystals, m. p. 105—107°, and dissolves in concentrated sulphuric acid, giving a yellow coloration which becomes red on addition of nitric acid. Its *acetyl* derivative, $C_{13}H_{16}O_6$, crystallises in small, colourless needles, m. p. 106°. The *benzoyl* derivative has m. p. 120—122°. 2:3:4:6-*Tetrahydroxyacetophenone tetramethyl ether*, $C_{12}H_{16}O_5$, has m. p. 43—45°, b. p. about 310°, and gives a yellow solution in concentrated sulphuric acid, which becomes intensely red when treated with nitric acid. Its *semicarbazone*, $C_{13}H_{19}O_5N_3$, forms small, colourless needles, m. p. 128—130°. 2′:3′:4′:6′-*Tetramethoxychalkone* (from benzaldehyde) crystallises in tufts of small, very pale yellow needles, m. p. 74—75° (softening at 70°). It dissolves in concentrated sulphuric acid with production of an orange-red coloration. 4:2′:3′:4′:6′-*Pentamethoxychalkone*, $C_{20}H_{22}O_6$ (from anisaldehyde), forms small, straw-yellow needles, m. p. 88—90° (previously softening), and dissolves in concentrated sulphuric acid with production of an orange-red coloration.

R. V. S.

α-Amino-ketones. SIEGMUND GABRIEL (*Ber.*, 1911, 44, 57—69).—A description is given of the preparation of some α-amino-ketones of the type $X{\cdot}CO{\cdot}CR_2{\cdot}NH_2$, hitherto unknown. *α-Phthaliminoisobutyric acid*, $C_6H_4<^{CO}_{CO}>N{\cdot}CMe_2{\cdot}CO_2H$, m. p. 153—154°, obtained from α-amino*iso*butyric acid and phthalic anhydride at 180°, is converted by phosphorus pentachloride into the *chloride*,

$$C_6H_4<^{CO}_{CO}>N{\cdot}CMe_2{\cdot}COCl,$$

m. p. 82—84°. By treatment with benzene and aluminium chloride, and subsequently with cold dilute hydrochloric acid, the chloride is converted into *α-phthaliminoisobutyrophenone*, m. p. 122—123·5°, which on hydrolysis by hot 10% potassium hydroxide and subsequent treatment with hydrochloric acid yields *α-aminoisobutyrophenone hydrochloride*, $COPh{\cdot}CMe_2{\cdot}NH_2,HCl,\frac{1}{2}H_2O$, sintering at about 137°; the anhydrous salt has m. p. 187—188°; the *picrate*, m. p. 175°. Unlike other α-amino-ketones, the salt of this new amino-ketone does not reduce Fehling's solution. *α-Aminoisobutyrophenone*, liberated from the hydrochloride by strong potassium hydroxide, has b. p. 254—255°/752 mm., and is the first α-amino-ketone that has been isolated in the pure state, others suffering condensation and oxidation to substituted pyrazines (Abstr., 1908, i, 464).

A suspension of ethyl sodiomalonate in benzene is treated with a benzene solution of α-phthaliminoisobutyryl chloride, and the yellow solution obtained is boiled for eighteen hours, neutralised by a little hydrochloric acid, and distilled with steam; the yellow residue is extracted

with ether (the insoluble yellow, crystalline powder is described in the following abstract), the ethereal filtrate, after being shaken with aqueous sodium carbonate, is evaporated, and the residue is dissolved in lukewarm amyl alcohol, the solution being kept for six hours at the ordinary temperature, whereby *ethyl α-phthaliminoisobutyryl-malonate*, $C_6H_4\langle^{CO}_{CO}\rangle N\cdot CMe_2\cdot CO\cdot CH(CO_2Et)_2$, m. p. 76—77·5°, is obtained. When boiled with hydriodic acid, b. p. 127°, for half an hour, the ester is decomposed into phthalic acid, carbon dioxide, ethyl iodide, and *methyl β-aminoisopropyl ketone hydriodide*,

$$CH_3\cdot CO\cdot CMe_2\cdot NH_2HI,$$

m. p. 169—170°. The *nitrate*, m. p. 132—133·5°, *hydrochloride*, m. p. 210—211°, *platinichloride*, m. p. 201° (decomp.), *aurichloride*, m. p. 165°, giving turbid liquid clarifying at 190°, *picrate*, m. p. 142—143·5°, *benzoyl* derivative, m. p. 124—125°, and *phthalyl* compound,

$$C_6H_4\langle^{CO}_{CO}\rangle N\cdot CMe_2\cdot COMe,$$

m. p. 105—106°, are described. The aqueous solutions of the salts of this α-amino-ketone do not reduce Fehling's solution. Unlike α-amino-*iso*butyrophenone, however, this amino-ketone cannot be isolated in a pure state. When an aqueous solution of its hydriodide is treated with an equivalent amount of *N*-sodium hydroxide, a certain amount of the amino-ketone is obtained together with a crystalline substance with an odour of menthol. The latter is obtained better by shaking the solid hydriodide with an excess of 33% potassium hydroxide; it has m. p. 88—89°, and is the hexahydrate of a *base*, $C_{10}H_{18}N_2$, b. p. 180—181°, m. p. 69—69·5°, which volatilises very readily and appears to be 2 : 3 : 3 : 5 : 6 : 6-*hexamethyl*-3 : 6-*dihydropyrazine*,

$$N\langle^{CMe\cdot CMe_2}_{CMe_2\cdot CMe}\rangle N;$$

its *hydrochloride*, *picrate*, m. p. 232° (decomp.), *platinichloride*, and *aurichloride*, decomp. 180°, are described. By reducing the base with sodium and alcohol, and treating the product with hydrochloric acid and potassium nitrite, *dinitrosohexamethylpiperazine*, $C_{10}H_{20}O_2N_4$, m. p. 248—249° (decomp.), is obtained, which is converted by boiling hydrochloric and a little acetic acids into *hexamethylpiperazine hydrochloride*, $C_{10}H_{22}N_2.2HCl$, from which the hydrated *base*, $C_{10}H_{22}N_2.2H_2O$, m. p. 65—66·5°, is obtained by the action of concentrated potassium hydroxide; the *nitrate*, *platinichloride*, *aurichloride*, *picrate*, decomp. 260°, and *mercurichloride* are mentioned. A by-product of the action of very concentrated potassium hydroxide on methyl β-amino*iso*propyl ketone hydriodide is a basic *substance*, $C_{10}H_{18}N_2$, which forms a *hydrochloride*, $C_{10}H_{18}N_2.2HCl,2H_2O$, m. p. about 171—172°, *platinichloride*, $C_{10}H_{18}N_2,H_2PtCl_6$, *benzoyl* derivative, $C_{10}H_{17}N_2Bz$, m. p. 105°, *picrate*, m. p. 198°, and *aurichloride*. Its constitution has not yet been ascertained; probably it is an aminopyrrole or pyridine derivative.

C. S.

The Beckmann Rearrangement. II. Mitsuru Kuhara and Yoshinori Todo (*Mem. Coll. Sci. Eng. Kyōto*, 1910, 2, 387—396).—The influence of acetyl chloride, chloroacetyl chloride, and benzene-

sulphonyl chloride on the rate of rearrangement of diphenylketoxime has been determined by heating a chloroform solution of the acid chloride and the oxime in molecular proportions at 60°, and weighing the benzanilide produced.

In ½-molar solutions, diphenylketoxime is almost completely transformed into benzanilide by benzenesulphonyl chloride in five minutes, whilst with chloroacetyl chloride, 61% undergoes change in the same time; in the case of acetyl chloride the rate of rearrangement is much slower, only 9·4% of the oxime being transformed in fifteen minutes.

The rates of rearrangement thus stand in the order of magnitude of the dissociation constants of the acids, and the conclusion is therefore drawn that the velocity of transformation of the oxime esters, $CPh_2{:}N{\cdot}O{\cdot}CO{\cdot}R$, is dependent on the negative character of the acid residue $R{\cdot}CO{\cdot}O$.

Measurements of the velocity of rearrangement of acetyldiphenylketoxime in the presence of hydrochloric acid, and of diphenylketoxime in the presence of acetyl chloride, both in ½-molar chloroform solutions, indicate that these reactions are unimolecular.

With respect to the mechanism of the rearrangement, the authors propose the following scheme:

$$\mathrm{Ph\,C\,Ph} \;\underset{\mathrm{N{\cdot}OH}}{\overset{\mathrm{AcCl}}{\xrightarrow{(1)}}}\; \mathrm{PhC(Cl)Ph} \;\underset{\mathrm{HCl\,N{\cdot}OAc}}{\xrightarrow{(2)}}\; \mathrm{PhC{\cdot}OAc} \;\underset{\mathrm{HCl\,NPh}}{\xrightarrow{(3)}}\; \mathrm{PhCO} \;\underset{\mathrm{HNPh}}{\xrightarrow{}}\; + \mathrm{AcCl},$$

in which the changes (1) and (3) take place rapidly, whilst the reaction (2) occurs slowly, thus accounting for the transformation being, apparently, of the unimolecular type.

According to the authors, the primary cause of the change:

$$\text{(I)}\ \mathrm{R{\cdot}C{\cdot}R}\ (\mathrm{N{\cdot}O{\cdot}COR'}) \longrightarrow \text{(II)}\ \mathrm{R{\cdot}C{\cdot}O{\cdot}COR'}\ (\mathrm{N{\cdot}R})$$

is the negative character of the acid residue $R'CO{\cdot}O$; with strongly negative residues, dissociation of (I) into $R_2C{:}N-$ and $R'CO{\cdot}O$ readily takes place, and these dissociation products then react to form (II).

It has been shown (Kuhara and Kainosho, Abstr., 1907, i, 1027) that the presence of hydrochloric acid is necessary for the rearrangement of acetyldiphenylketoxime, and the authors therefore draw the conclusion that in the case of the oxime-acetates, hydrochlorides of the type $CR_2{:}N{\cdot}OAc,HCl$ are produced; under the influence of the hydrochloric acid, the tendency of the OAc group to separate from the nitrogen atom is increased to such an extent that a similar dissociation to that mentioned above takes place.

A *compound* of the constitution $OAc{\cdot}CPh{:}NPh$ has been obtained as a viscid, yellow oil by the interaction of the imide-chloride, $CPhCl{:}NPh$, and silver acetate. On passing hydrochloric acid into its cold ethereal solution, the *hydrochloride* separates out as a canary-yellow precipitate, which is converted by excess of the acid into acetylbenzanilide. When the hydrochloride in chloroform solution is heated above 60°, it yields benzanilide. This change corresponds with the last phase of the rearrangement in the authors scheme given above.

F. B.

Ketens. XV. Action of Diphenylketen on Nitroso-compounds. HERMANN STAUDINGER and SERGIUS JELAGIN (*Ber.*, 1911, 44, 365—374. Compare Abstr., 1910, i, 46).—By the action of nitrosodimethylaniline in ethereal solution in 2 mols. of diphenylketen, carbon dioxide is liberated, the green colour at once vanishes, and the Schiff's base first formed combines with diphenylketen to form a *β-lactam* of *β-dimethylaminoanilino-aaββ-tetraphenylpropionic acid*, $CPh_2<^{CO}_{CPh_2}>N\cdot C_6H_4\cdot NMe_2$. This forms colourless crystals, which sinter at 196°, m. p. above 200° (decomp. to an orange-red liquid). The composition of this lactam was proved by its synthesis from diphenylketen and benzophenone *p*-dimethylaminoanil.

Nitrosobenzene reacts differently with diphenylketen, forming *anhydrodiphenylglycollylphenylhydroxylamine*, $CPh_2<^{CO}_{O}>NPh$, which separates in well formed, colourless crystals, m. p. 72·5°. It is stable at the melting point, but, on further heating, decomposes explosively into benzophenone and phenylcarbimide. When boiled with concentrated hydrochloric acid, *chlorodiphenylacetophenylhydroxylamine*, $CPh_2Cl\cdot CO\cdot NPh\cdot OH$, colourless crystals, m. p. 158·5—159·5°, is formed. The four-membered ring-compound is obtained synthetically by the action of chlorodiphenylacetyl chloride on phenylhydroxylamine.

Nitrosobenzene and 2 mols. of diphenylketen also react to form small quantities of the *β-lactam* of *β-anilino-aaββ-tetraphenylpropionic acid*, $CPh_2<^{CO}_{CPh_2}>NPh$, m. p. 191°, which is also formed on condensing benzophenoneanil with diphenylketen. The four-membered ring, $CPh_2<^{CO}_{NPh}>O$, is possibly formed in small quantity during the action of nitrosobenzene on diphenylketen, but decomposes in the cold into benzophenoneanil and carbon dioxide.

Diphenyl- and dimethyl-nitrosoamines do not react with diphenylketen. E. F. A.

Action of Nitric Acid on Halogen Derivatives of *o*-Alkylated Phenols. II. THEODOR ZINCKE and W. BREITWEISER (*Ber.*, 1911, 44, 176—184).—The products formed by the action of nitric acid on tribromo-*p*-xylenol are similar to those obtained previously from tetrabromo-*o*-cresol (Abstr., 1907, i, 322). They are three in number, namely: (*a*) 3 : 5 : 6-tribromo-1 : 4-dimethylquinonitrole,

$$CMe<^{CBr\cdot CO}_{CBr:CBr}>CMe\cdot NO_2.$$

(*b*) An additive compound of the quinonitrole with nitric acid,

$$CMe<^{CBr\cdot C(OH)(O\cdot NO_2)}_{CBr\quad\quad CBr}>CMe\cdot NO_2.$$

(*c*) An open-chain compound, $NO_2\cdot CHMe\cdot CBr:CBr\cdot CMe:CBr\cdot CO\cdot ONO_2$, which can also be obtained by the action of sodium carbonate solution on the additive compound.

The quinonitrole is identical with the product described by Auwers (Abstr., 1899, i, 30), but is regarded as an ortho- and not a para-

derivative, since the quinole obtained by the action of cold benzene on the nitro-compound does not lose hydrogen bromide and form dibromo-*p*-xyloquinone, and does not yield a *p*-xyloquinone derivative when heated with sodium acetate and acetic anhydride, but loses nitrous acid extremely readily under the influence of moist ether, yielding 3 : 5 : 6-tribromo-4-methyl-*o*-methylenequinone,

$$CMe\begin{matrix}<CBr{:}CBr\\ CBr{\cdot}CO-\end{matrix}>C{:}CH_2.$$

The conversion of the quinonitrole into dibromo-*p*-xyloquinone by boiling with benzene or light petroleum, and of the quinole into dibromo-*p*-xyloquinone by warming with acetic anhydride and concentrated sulphuric acid is accompanied by molecular rearrangements.

3 : 4 : 6-Tribromo-1 : 4-dimethylquinonitrole is most readily prepared by the action of concentrated nitric acid on tribromo-*p*-xylenol in the presence of glacial acetic acid. It reacts with cold methyl alcohol, yielding 3 : 6-*dibromo*-5-*nitro*-p-2-*xylenol*, $NO_2{\cdot}C_6Me_2Br_2{\cdot}OH$, as colourless needles, m. p. 154°, together with a product, m. p. 186—190°, insoluble in alkalis, and with acetic anhydride and a few drops of concentrated sulphuric acid yields *dibromo-p-xyloquinol diacetate* in the form of yellowish white needles, m. p. 218°. 3 : 5 : 6-*Tribromo*-1 : 4-*dimethylquinol*, $C_8H_7O_2Br_3$, crystallises from light petroleum in colourless needles, m. p. 111°.

3 : 5 : 6-*Tribromo*-4-*methyl*-*o*-*methylenequinone*, $C_8H_5OBr_3$, crystallises from acetic anhydride in yellow plates, m. p. 220—230° (decomp.), and is not chemically active. The *acetyl* derivative of 3 : 6-dibromo-5-nitro-*p*-2-xylenol crystallises in colourless, glistening prisms, m. p. 116°, and 3 : 6-*dibromo*-4-*amino*-p-2-*xylenol* crystallises from benzene in colourless plates, m. p. 186—188°. The additive *compound* of the quinonitrole with nitric acid, $C_8H_7O_6N_2Br_3$, crystallises in colourless, well-developed prisms, m. p. 105—107° (decomp.). The open-chain *compound*, $C_8H_7O_6N_2Br_3$, crystallises in colourless needles, m. p. 141° (decomp.). J. J. S.

Oxidation of Aniline. II. Riko Majima (*Ber.*, 1911, **44**, 229—234. Compare Willstätter and Majima, Abstr., 1910, i, 748).—By the oxidation of aniline with sodium bromate in aqueous acetic acid solution at 0°, a mixture of 2 : 5-dianilino-*p*-benzoquinoneanil and *amino-anilino*-p-*benzoquinoneanil*,

$$O{:}C\begin{matrix}<CH{=}{=}C(NH_2)\\ C(NHPh){:}CH\end{matrix}>C{:}NPh \text{ or } O{:}C\begin{matrix}<C(NH_2){=}{=}CH\\ CH{:}C(NHPh)\end{matrix}>C{:}NPh,$$

is produced. The latter compound, isolated by means of its sparingly soluble *sulphate*, crystallises in bluish-red prisms. It dissolves in concentrated sulphuric acid with a green colour, has feebly basic properties, and yields 2 : 5-dianilino-*p*-benzoquinoneanil when heated with aniline in glacial acetic acid solution. The *hydrochloride*, $C_{18}H_{15}ON_3{,}HCl$, forms dark green crystals.

2 : 5-Dianilino-*p*-benzoquinoneimine (Willstätter and Majima, *loc. cit.*) is more conveniently prepared by oxidising aniline with sodium persulphate. When hydrolysed with hydrochloric acid in aqueous alcoholic solution, it yields 2 : 5-dianilino-*p*-benzoquinone. F. B.

Synthesis of β-Menthol-lactoside and its Behaviour in the Organism. HANS FISCHER (*Zeitsch. physiol. Chem.*, 1911, 70, 256—263. Compare E. and H. Fischer, Abstr., 1910, i, 716).—*Hepta-acetyl-β-menthol-lactoside*, prepared by the interaction of aceto-bromolactose and menthol in presence of silver carbonate and chloroform, crystallises in long prisms, m. p. 125—130°, $[\alpha]_D^{19}$ −29·65° (±0·2). It resists hydrolysis by dilute mineral acids; barium hydroxide converts it into *β-menthol-lactoside*. This crystallises with $4H_2O$ in concentrically-grouped prismatic needles, m. p. 110°, $[\alpha]_D^{15}$ −38·04°. It is hydrolysed by mineral acids to menthol and reducing sugar, and by emulsin to menthol, lactose, and some dextrose. Kephir lactose hydrolyses it slowly.

When injected subcutaneously into the organism, it is excreted unchanged; neither mentholglycuronic acid nor menthol-lacturonic acid are formed.

Mentholglycuronic acid ($1\frac{1}{2}H_2O$) sinters at 92°, m. p. 110°, and has $[\alpha]_D^{20}$ −104·4°. E. F. A.

Some Derivatives of Dicamphor. VINCENZO CASTELLANA and R. FERRERO (*Gazzetta*, 1910, 40, ii, 482—491. Compare Angeli, Castellana, and Ferrero, Abstr., 1909, i, 739).—When pernitrosodicamphor is boiled with an excess of alcoholic potassium hydroxide, the *potassium* salt separates as a precipitate. If water is added to dissolve this, the boiling continued for an hour, and then the alcohol removed by distillation, *dicamphenoneimine* remains as an oil, which on cooling solidifies and after recrystallisation forms needles, m. p. 191°. If the ebullition is prolonged for several hours, an amorphous, grey powder having the properties of an *acid* is obtained on acidifying the wash water of the preceding compound. To the imine the structure $C_8H_{14}<\begin{matrix}C=\!\!=\!\!=C\\ |\quad\quad |\\ C{:}NH\quad OC\end{matrix}>C_8H_{14}$ is ascribed. It forms a *picrate*, $C_{20}H_{29}ON,C_6H_2(NO_2)_3OH$, m. p. 195°. When warmed with dilute sulphuric acid, the imine yields the corresponding diketone, *dicamphenone*, $C_8H_{14}<\begin{matrix}C=\!\!=\!\!=C\\ |\quad\quad |\\ CO\quad OC\end{matrix}>C_8H_{14}$, which crystallises in lemon-yellow needles, m. p. 192—193°, and is identical with the dicamphanehexanedione of Oddo (Abstr., 1897, i, 577). With hydrazine, it yields the azine, as stated by that author, and at the same time a small quantity of a yellow *substance*, m. p. 153°, is formed. The same azine is obtained from hydrazine and pernitrosodicamphor. Its *picrate*, $C_{20}H_{28}N_2,C_6H_2O_7N_3$, has m. p. 220°.

Pernitrosodicamphor when treated with an excess of hydroxylamine yields two products which can be separated with the aid of solvents, and are apparently stereoisomeric *dioximes*, $C_{20}H_{32}O_2N_2$. One is crystalline, and has m. p. about 240° (decomp.); the other is formed in very small amount, and has m. p. about 275—280°.

The authors have also prepared pernitrosocamphor and some of its derivatives from inactive camphor, and find them to have similar properties, but somewhat lower melting points: *pernitroso-i-camphor* has m. p. 32°; *pernitrosodi-i-camphor*, m. p. 163°; *i-dicamphenoneimine*, m. p. 179°. R. V. S.

Behaviour of Iodine towards Terpine Hydrate, Eucalyptol, and Terpineol. CARLO CASANOVA (*Boll. chim. farm.*, 1910, 49, 957—960. Compare Abstr., 1909, i, 813).—The above terpenes react with iodine on warming, and the liquid compounds produced are heavier than water and give no reaction with starch. They readily decompose in the course of a few hours if exposed to light and air, large quantities of iodine and hydrogen iodide being set free.

R. V. S.

Constituents of Ethereal Oils. Constitution of Perillaldehyde, $C_{10}H_{14}O$. FRIEDRICH W. SEMMLER and B. ZAAR (*Ber.*, 1911, 44, 52—57).—The aldehyde isolated from *Perilla nankinensis* leaf oil, and described by Schimmel & Co. (Abstr., 1910, i, 758), has been isolated and examined by the authors. In addition to the properties already recorded (*loc. cit.*), the aldehyde, which is called perillaldehyde, shows the following behaviour. The *semicarbazone* has m. p. 199—200°. By reduction with zinc dust and glacial acetic acid on the water-bath, the aldehyde yields perillyl alcohol in the form of its *acetate*, $C_{12}H_{18}O_2$, b. p. 123—126°/13 mm., D^{20} 0·9785, n_D 1·48142, $[\alpha]_D$ −48°; the *alcohol*, $C_{10}H_{16}O$, obtained by hydrolysing the ester by alcoholic potassium hydroxide, has b. p. 119—121°/11 mm., D^{20} 0·9640, n_D 1·49964, $[\alpha]_D$ −68·5°, and is converted by phosphorus pentachloride in petroleum solution into the *chloride*, $C_{10}H_{15}Cl$, b. p. 99—101°/12 mm., D^{20} 0·9861, n_D 1·49728, $[\alpha]_D$ −60°. By treatment with sodium and alcohol, the chloride is converted into *l*-limonene.

Perillaldoxime is changed by boiling acetic anhydride and sodium acetate into *perillonitrile*, $C_{10}H_{13}N$, b. p. 116—118°/11 mm., D^{20} 0·9439, n_D 1·49775, $[\alpha]_D$ −115°, which by hydrolysis yields *perillic acid*, $C_{10}H_{14}O_2$, b. p. 164—165°/10 mm., m. p. 130—131°, $[\alpha]_D$ −20° in 25% alcoholic solution. The acid forms a *dibromide*, $C_{10}H_{14}O_2Br_2$, m. p. 166—167°, and is reduced by sodium and boiling amyl alcohol to *dihydroperillic acid*, $C_{10}H_{18}O_2$, b. p. 152—153°/10·5 mm., m. p. 107—109°, $[\alpha]_D$ 0° in 25% alcoholic solution, which forms a *dibromide*, m. p. 116—117°, and a *methyl* ester (from the silver salt and methyl iodide), b. p. 105—106°/11 mm., D^{18} 0·9732, n_D 1·46768, $[\alpha]_D$ 0°, from which *dihydroperillyl alcohol*, $C_{10}H_{18}O$, b. p. 114—115°/10 mm., D^{19} 0·9284, n_D 1·48191, $[\alpha]_D$ 0°, is obtained by the action of sodium in the usual way.

The formation of the preceding derivatives, particularly of *l*-limonene, and the fact that the molecular refraction of perillaldehyde indicates the presence of two ethylenic linkings, afford good evidence of the constitution $CH_2{:}CMe{\cdot}CH\begin{matrix}<\\>\end{matrix}\begin{matrix}CH_2{\cdot}CH_2\\CH_2{-}CH\end{matrix}C{\cdot}CHO$ for the aldehyde.

C. S.

Curcumin. C. LORING JACKSON and LATHAM CLARKE (*Amer. Chem. J.*, 1911, **45**, 48—58).—Miłobędzka, Kostanecki, and Lampe's statement (Abstr., 1910, i, 629) that curcumin should be represented by the formula $C_{21}H_{20}O_6$, first proposed by Ciamician and Silber (Abstr., 1897, i, 229), instead of $C_{14}H_{14}O_4$, as suggested by Jackson and Menke (*Amer. Chem. J.*, 1884, **4**, 77), is confirmed. Curcumin has m. p. 178°,

as found by Jackson and Menke, and not 183°, as stated by Ciamician and Silber. Curcumin dimethyl ether has m. p. 137°, instead of 135°, as recorded by Ciamician and Silber, and can be obtained in a quantitative yield by using a shaking machine instead of applying heat.

The brown coloration produced by the action of hydrogen chloride on curcumin is due to the formation of an additive *compound*, which is dark brown when only a little hydrogen chloride is used, but becomes dark violet when an excess is employed; it is very unstable, and is instantly decomposed by water. A similar *compound*,

$$C_{21}H_{20}O_6,3HBr,$$

is formed by the action of hydrogen bromide. The reddish-purple substance formed by the action of phosphoryl chloride on curcumin (Jackson and Menke, *loc. cit.*) is probably either the hydrogen chloride additive compound or a similar product containing chlorine and phosphorus, since it is reconverted into curcumin by the action of water. This substance, if left in a desiccator, becomes black, owing to the further action of the phosphoryl chloride.

When an alcoholic solution of curcumin is shaken for a long time with hydroxylamine hydrochloride, a *compound*, m. p. 162°, probably the mono-oxime, is produced, which forms stout, orange-yellow needles. If the mixture is heated on the steam-bath instead of being shaken at the ordinary temperature, a yellowish-white compound, m. p. 163°, is obtained, which is probably identical with the foregoing, although of a different colour. This substance is not identical with the *iso*oxazole described by Ciamician and Silber (*loc. cit.*). E. G.

Pyronone Synthesis by means of the "Tertiary Bases Reaction." II. EDGAR WEDEKIND [and JOHANNES HAUSSERMANN, W. WEISSWANGE, and MORIZ MILLER] (*Annalen*, 1911, 378, 261—292).—The "tertiary bases reaction" (Wedekind and Häussermann, Abstr., 1908, i, 671) has been applied to phenylacetyl chloride, phenylpropionyl chloride, *p*-nitrophenylacetyl chloride, and butyryl chloride; pyronone derivatives are formed, the production of a diketo-*cyclo*butane, as in the case of *iso*butyryl chloride (Wedekind and Weisswange, Abstr., 1906, i, 437), not being observed.

Thus by slowly adding a solution of phenylacetyl chloride (1 mol.) in dry carbon disulphide to a solution of a tertiary base (tripropylamine, pyridine, 1-methylpiperidine, or, best of all, triethylamine) in the same solvent at 0°, moisture being rigorously excluded by passing a slow stream of dry hydrogen through the apparatus, 3 : 5-*diphenyl*-2-*benzyl*-1 : 4 : 6-*pyronone*, $CO<\begin{matrix}CHPh\text{——}CO\\CPh{:}C(CH_2Ph)\end{matrix}>O$, m. p. 173—174°, is obtained in 50% yield, its formation being explained in the same way as that of 3 : 5-dimethyl-2-ethyl-1 : 4 : 6-pyronone from propionyl chloride (Wedekind and Häussermann, *loc. cit.*). The substance is remarkably stable to reducing agents, behaves as a monobasic acid (*sodium* salt, $C_{24}H_{17}O_3Na,3EtOH$, colourless crystals from alcohol), but not as an oxonium base, and is decomposed by 20% potassium hydroxide into diphenylacetone, phenylacetic acid, and carbon dioxide. This reaction suggests that the substance might be *s*-triphenylphloro-

glucinol, produced by the polymerisation of 3 mols. of phenylketen. Its pyronone constitution, however, is indicated by the formation of a *mono-oxime*, m. p. 157° (decomp.), *acetate*, $C_{26}H_{20}O_4$, m. p. 124—125°, and *benzoate*, $C_{31}H_{22}O_4$, m. p. 126°, by the non-formation of triphenylbenzene by reduction with zinc dust, and by its behaviour with concentrated aqueous ammonia at 80—100° and finally at 130—140°, whereby 4 : 6-*dihydroxy*-3 : 5-*diphenyl*-2-*benzylpyridine*,

$$N<\begin{matrix}C(CH_2Ph):CPh\\ C(OH)=\!=CPh\end{matrix}>C\cdot OH,$$

m. p. 260°, is obtained. This substance has acidic properties, does not decolorise bromine, develops a reddish-brown coloration with alcoholic ferric chloride (distinction from the pyronone), and forms a *diacetate*, m. p. 165°. The ready formation of an oxime from diphenylbenzylpyronone is unusual; its oximic structure is proved by the regeneration of hydroxylamine and the pyronone by hydrolysis with concentrated hydrochloric acid.

Phenylpropionyl chloride and tripropylamine, reacting under the preceding conditions, yield 3 : 5-*dibenzyl*-2-*β*-*phenylethyl*-1 : 4 : 6-*pyronone*, $CH_2Ph\cdot CH_2\cdot C<\begin{matrix}C(CH_2Ph)\cdot CO\\ O\text{———}CO\end{matrix}>CH\cdot CH_2Ph$, m. p. 167—168°, which resembles diphenylbenzylpyronone, but is less acidic, does not form an oxime, and is more readily decomposed by 25% potassium hydroxide at 120°, yielding dibenzylacetone, phenylpropionic acid, and carbon dioxide.

Butyryl chloride and triethylamine react in carbon disulphide to form a pyronone derivative, which is so unstable, however, that its production is indicated only by the formation of dipropyl ketone resulting from its decomposition.

p-*Nitrophenylacetyl chloride*, b. p. 135—138°/0·1 mm., m. p. 47°, obtained from the acid and phosphorus pentachloride, reacts with triethylamine in dry ether cooled by a freezing mixture, 3 : 5-*di*-p-*nitrophenyl*-2-p-*nitrobenzyl*-1 : 4 : 6-*pyronone*,

$$NO_2\cdot C_6H_4\cdot CH_2\cdot C<\begin{matrix}C(C_6H_4\cdot NO_2)\cdot CO\\ O\text{———}CO\end{matrix}>CH\cdot C_6H_4\cdot NO_2,$$

m. p. 146° (decomp.), a yellow, microcrystalline powder, being produced, which has pronounced acidic properties and is decomposed by 20% potassium hydroxide at 160°, yielding *p*-nitrophenylacetic acid and pp′-*dinitrodiphenylacetone*, decomp. 205—206° (*phenylhydrazone*, decomp. 110—112°).

The "tertiary bases reaction" has also been applied to *iso*valeryl chloride and crotonyl chloride; the former with ethereal tripropylamine yields ethyl *iso*valerate and *iso*valeric anhydride, whilst the latter with triethylamine in benzene forms crotonic anhydride.

C. S.

"Oxindigo" [2:2′-Diketo-$\Delta^{1:1'}$-dicoumaran]. Richard Stoermer and K. Brachmann (*Ber.*, 1911, **44**, 315—319).—The yellow substance, m. p. 276° (decomp.), obtained by acidifying the potassium salt of *aci*-nitrocoumaranone and formerly regarded as "leuco-oxindigo" (Abstr., 1909, i, 174), is now found to be 2 : 2′-diketo-$\Delta^{1:1'}$-dicoumaran itself, since it is produced from the potassium salt by the action of iodine in

aqueous potassium iodide or alcohol, a reaction in which the formation of "leuco-oxindigo" [2 : 2′-dihydroxy-1 : 1′-dicoumaran] is impossible. The properties of the substance correspond almost exactly with those of 2 : 2′-diketo-$\Delta^{1:1'}$-dicoumaran prepared by Fries and Hasselbach (this vol., i, 150).

The action of chlorine water on potassium *aci*-nitrocoumaranone yields 1-*chloro*-1-*nitrocoumaranone*, $C_8H_4O_4NCl$, m. p. 102°. 1-*Bromo*-1-*nitrocoumaranone*, m. p. 105°, is obtained by shaking the potassium salt with bromine in benzene, or by rapidly adding bromine water to its aqueous solution; when the bromine water is added very slowly, diketo-$\Delta^{1:1'}$-dicoumaran is produced. C. S.

Coffee. IV. K. Gorter (*Annalen*, 1911, 379, 110—130. Compare Abstr., 1908, i, 186, 345).—The author replies to Lendrich and Nottbohm's criticism (Abstr., 1909, ii, 449) of his method for the estimation of the caffeine in raw coffee (*loc. cit.*), and describes experiments which show that the caffeine in Liberian coffee is all present as potassium caffeine chlorogenate.

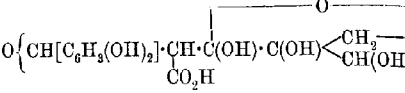
All formulæ previously suggested for hemichlorogenic acid are withdrawn and are replaced by the constitution given below for the following reasons: (1) In its fission by acids and alkalis, hemichlorogenic acid behaves like a β-ketonic acid. (2) The non-formation of an oxime, phenylhydrazone, and semicarbazone indicates the absence of a carbonyl group. (3) If the tetrahydropyrone formula previously suggested is correct, the acid should yield 3′ : 4′-dihydroxyflavone by the elimination of $3H_2O$ and of the carboxyl group. This result has not been effected by heating chlorogenic acid with hydriodic acid, with water at 220—230°, or alone at 240—250° in a vacuum. (4) By treatment with bromine (1 mol.) in chloroform in sunlight, penta-acetylhemichlorogenic acid yields a crystalline, additive *compound*, $C_{16}H_{13}O_9Ac_5Br_2$, m. p. 214—215°, which cannot be acetylated, quantitatively regenerates penta-acetylhemichlorogenic acid with alcohol and potassium iodide, and is converted by boiling potassium hydroxide into quinic and bromocaffeic acids. (5) The fact that only five of the six hydroxyl groups in hemichlorogenic acid can be acetylated is proved by showing by Zerewitinoff's method with magnesium methyl iodide in amyl ether that penta-acetylhemichlorogenic acid, which cannot be further acetylated even by acetyl chloride in pyridine, still contains a hydroxyl group. If hemichlorogenic acid were identical with α-quinylcaffeic acid,

$$C_6H_3(OH)_2\cdot CH{:}C(CO_2H)\cdot CO\cdot C(OH)<\begin{matrix}CH_2\cdot CH(OH)\\ CH(OH)\cdot CH_2\end{matrix}>CH\cdot OH,$$

the non-acetylated hydroxyl group would be the tertiary one, a view which is untenable, since this group in quinic acid itself is easily acetylated. (6) Chlorogenic and penta-acetylhemichlorogenic acids are not reduced by zinc dust and acetic acid, and therefore do not contain an ethylenic linking in the $\alpha\beta$-position to a carbonyl group. For these reasons and others already recorded, hemichlorogenic acid is represented by the constitution:

$$C_6H_3(OH)_2\cdot CH{:}C(CO_2H)\cdot \overset{*}{C}(OH)\cdot C(OH)<\begin{matrix}CH_2\text{——}O\\ CH(OH)\cdot CH_2\end{matrix}>CH\cdot OH,$$

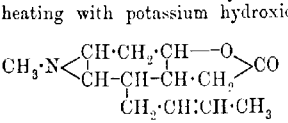
in which the * denotes the hydroxyl group which cannot be acetylated. Consequently, chlorogenic acid has the constitution:



which is in harmony with the result obtained by reducing the acid by sodium amalgam in a solution which is kept slightly acidic by the continuous addition of sulphuric acid. The product of reduction is *dihydrohemichlorogenic acid*, $C_{16}H_{20}O_9$, m. p. 167—168°, which forms a *penta-acetate*, m. p. 182°, and is decomposed by hydrochloric acid or potassium hydroxide into quinic acid and *dihydrocaffeic acid*, $C_9H_{10}O_4$, m. p. 139°. Its formation is explained by the conversion of the chlorogenic acid into hemichlorogenic acid, which, as an $\alpha\beta$-unsaturated acid, is easily reduced to the dihydro-compound. C. S.

Dioscorine. K. Gorter (*Chem. Zentr.*, 1910, ii, 1228—1229, from *Ann. Jardin Bot. Buitenzorg.*, 1909, [ii], Suppl. 3, 385—392).—From the bulbs of *Dioscorea hirsuta*, Boorsma, and later Schutte (Abstr., 1898, i, 341), isolated a crystalline alkaloid, dioscorine, $C_{13}H_{19}O_2N$. The base was isolated from the bulbs by extraction with alcohol acidified with acetic acid; it can be distilled unchanged in a vacuum. The following salts are described: *hydrobromide*, white crystals, m. p. 213—214°; *oxalate*, white prisms, m. p. 69·5—70·5°; *methiodide*, m. p. 213°; *methochloride aurichloride*, plates, m. p. 188°; *methochloride platinichloride*, orange tufts, m. p. 218°.

Dioscorine is not acted on by acetic anhydride, and it must be considered to be a tertiary base not containing an OH group. On heating with potassium hydroxide it gives a *potassium* salt, which again yields dioscorine by the action of hydrochloric acid. It must therefore be considered that dioscorine is a γ-lactone. When dioscorine is heated with concentrated potassium hydroxide at 200—250° in the presence of air, methylamine is evolved; dioscorine methiodide gives dimethylamine under similar conditions, a phenol-like substance being also formed. An acid solution of potassium permanganate is at once decolorised by dioscorine. The annexed constitution for dioscorine is suggested. N. C.



Alkaloid of Eschscholtzia Californica. Georges Brindejonc (*Bull. Soc. chim.*, 1911, [iv], **9**, 97—100).—This plant contains 0·25% of a new alkaloid, ionidine. No other alkaloid is present (compare R. Fischer, Abstr., 1901, i, 743).

An alcoholic extract of the plant deposits potassium nitrate on concentration, and when extracted with warm water deposits resin. From the filtrate after defæcation with lead acetate and addition of alkali, ether extracts *ionidine*, $C_{19}H_{25}O_4N_4$, m. p. 154—156°, which crystallises in short, flattened, colourless, transparent prisms. Its solubility in cold alcohol (90°) is 0·46%, and in water 1 in 2500. The alkaloid is strongly basic, and yields bitter, very soluble, gummy salts

with acids. The *aurichloride, platinichloride,* and *mercurichloride* are all amorphous. It is precipitated from dilute solutions by iodine, picric acid, or gold chloride, and gives characteristic colour reactions with various reagents, of which the most useful are the following: sulphuric acid gives no coloration, but with sulphuric acid containing a *trace* of nitrous acid, a deep violet tint is produced, and a similar coloration is given with Fröhde's reagent. In both cases the violet tint changes to brown when kept. T. A. H.

Codeine Oxide. GUSTAV MOSSLER and ERICH TSCHEBULL (*Ber.*, 1911, **44**, 105—109).—By not too prolonged treatment with 1·5% hydrogen peroxide on the water-bath, codeine yields a bimolecular *codeine oxide*, $C_{36}H_{44}O_9N_2,7H_2O$, m. p. 200—202° (decomp.), crystallising in elongated, rectangular plates. The substance loses $6H_2O$ in a vacuum, and $7H_2O$ at 100—110°, and then has m. p. 211—215° (decomp.). It contains two atoms of active oxygen; the monohydrate has $[\alpha]_D$ −97·6° in water and −105·9° in 97% alcohol, the values for the anhydrous substance being −99·6° and −107·2°. The molecular weight is determined by the ebullioscopic method in water.

The *hydrochloride*, $C_{18}H_{21}O_4N,HCl,H_2O$, obtained by treating a hot alcoholic solution of the bimolecular oxide with hydrochloric acid, has m. p. 219—220° when anhydrous, and has $[\alpha]_D$ −105·8° in water. By treating its aqueous solution with sodium carbonate, the hydrochloride yields a unimolecular *oxide*, $C_{18}H_{21}O_4N,H_2O$, m. p. 215°, $[\alpha]_D$ −97·1° in water (compare Freund and Speyer, this vol., i, 76).

C. S.

Aldehyde Sulphites of Vegetable Alkaloids. MARIO MAYER (*Gazzetta*, 1910, **40**, ii, 402—414).—*Brucine benzaldehyde sulphite*,

$$C_{23}H_{26}O_4N_2,H_2SO_3,C_7H_6O,$$

is prepared by treating a suspension of brucine in water with sulphur dioxide until solution is complete, and then shaking the liquid with benzaldehyde. It forms a colourless, crystalline precipitate, m. p. 125° (decomp.). The following similar compounds were prepared in the same way. The analytical figures mostly indicate an excess of alkaloid. *Brucine anisaldehyde sulphite*, $C_{23}H_{26}O_4N_2,H_2SO_3,C_8H_8O_2$, is a white powder, which softens at 108° and decomposes at 115°. *Brucine salicylaldehyde sulphite*, $C_{23}H_{26}O_4N_2,H_2SO_3,C_7H_6O_2$, is a colourless powder, decomposing at 120°. *Brucine heptaldehyde sulphite*,

$$C_{23}H_{26}O_4N_2,H_2SO_3,C_7H_{14}O,$$

is a white, crystalline substance, decomposing at 102°. *Brucine propaldehyde sulphite*, $C_{23}H_{26}O_4N_2,H_2SO_3,C_3H_6O$, separates only when the solution is kept in presence of sulphuric acid; it decomposes at 35°. *Brucine acetone sulphite*, $C_{23}H_{26}O_4N_2,H_2SO_3,C_3H_6O$, is a colourless, crystalline substance, decomposing at 190°. *Brucine benzophenone sulphite*, $C_{23}H_{26}O_4N_2,H_2SO_3,C_{10}H_{10}O$, is prepared in alcoholic solution; it is a colourless, crystalline substance, decomposing at 120°. *Brucine acetophenone sulphite*, $C_{23}H_{26}O_4N_2,H_2SO_3,C_8H_8O$, forms a yellow, crystalline powder, decomposing at 108°.

Brucinic acid benzaldehyde sulphite, $C_{23}H_{28}O_5N_2,H_2SO_3,C_7H_6O$, crystallises in clusters of small needles, decomposing at 122°.

Brucinic acid ethiodide, $C_{25}H_{33}O_5N_2I,H_2O$, prepared by the method

used by Moufang and Tafel (Abstr., 1899, i, 309) for the methyl derivative, is a grey mass, m. p. 205° (decomp.). It yields with sulphur dioxide and benzaldehyde a small quantity of a *substance*, m. p. 145° (decomp.), which does not contain iodine.

Berberine sulphite is obtained by acting on the hydrochloride with a saturated solution of sulphur dioxide in concentrated sodium hydrogen sulphite (compare Perkin, Trans., 1890, 57, 1097). When to a solution of the salt in the cold, benzaldehyde and alcohol are added and the liquid is treated with sulphur dioxide, *berberine benzaldehyde sulphite*, $C_{20}H_{17}O_4N,H_2SO_3,C_7H_6O$, is obtained in golden-yellow, silky needles, which become brown at 180°. *Morphine benzaldehyde sulphite*, $C_{17}H_{19}O_3N,H_2SO_3,C_7H_6O$, is a crystalline substance, m. p. 115° (decomp.). *Narcotine benzaldehyde sulphite*, $C_{22}H_{23}O_7N,H_2SO_3,C_7H_6O$, is a colourless, crystalline powder, m. p. 70° (partial decomp.). *Cocaine benzaldehyde sulphite*, $C_{17}H_{21}O_4N,H_2SO_3,C_7H_6O$, is obtained in alcoholic solution, and forms a colourless, deliquescent mass.

Quinine benzaldehyde sulphite, $C_{20}H_{24}O_2N_2,2H_2SO_3,2C_7H_6O$, prepared in alcoholic solution, is a powder which decomposes at 85°, and at ordinary temperatures and pressures evolves sulphur dioxide. *Cinchonine benzaldehyde sulphite*, $C_{19}H_{22}ON_2,2H_2SO_3,2C_7H_6O$, forms a white powder which decomposes at 90°, and loses sulphur dioxide when kept in a desiccator.

Benzaldehyde anhydrosulphites of the alkaloids are obtained when chloroform or benzene solutions of the alkaloids are treated with dry sulphur dioxide, and benzaldehyde is subsequently added. The anhydrosulphites appear as crystalline or resinous residues when the liquids are evaporated, and have properties similar to those of the sulphites. *Pilocarpine benzaldehyde anhydrosulphite*,

$$C_{11}H_{16}O_2N_2,SO_2,C_7H_6O,$$

is a colourless, crystalline substance, decomposing at 105°. The *narcotine* compound, $C_{22}H_{23}O_7N,SO_2,C_7H_6O$, is also colourless and crystalline; it decomposes at 80°. The *brucine* compound, $C_{23}H_{26}O_4N_2,SO_2,C_7H_6O$, is crystalline, and has m. p. 105° (decomp.). It dissolves readily in water, the sulphite being precipitated. The *brucinic acid compound*, $C_{23}H_{25}O_5N_2,SO_2,C_7H_6O$, is a crystalline mass, decomposing at 95°. *Strychnine*, although a monoacidic base, yields an anhydrosulphite to which the formula $C_{21}H_{22}O_2N_2,2SO_2,2C_7H_6O$ may be ascribed, although the analytical figures differ somewhat from those required by this formula. The substance is a yellow, resinous mass, m. p. 110° (decomp.), which continually evolves sulphur dioxide. When dissolved in water it loses sulphur dioxide and benzaldehyde, and on evaporation of the solution a solid resin is obtained, m. p. 95° (decomp.), which is probably *strychnine benzaldehyde sulphite*, $C_{21}H_{22}O_2N_2,H_2SO_3,C_7H_6O$.

It is suggested that the sulphites described in this paper have the structure $C_nH_m{\cdot}CH\langle{}^{O}_{SO_2}{>}N{:}R$, N:R representing the alkaloid.

R. V. S.

Action of Sulphuryl Chloride on *s*-Dimethylpyrrole. U. Colacicchi (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 645—648).—Sulphuryl chloride (2 mols.) reacts with 2 : 5-dimethylpyrrole in

ethereal solution at 0°. The liquid, after remaining for two days at the ordinary temperature, was treated with ice, and the residue from the ethereal solution was subjected to steam distillation. No distillate was obtained, but the aqueous residue in the distilling vessel deposited crystals on cooling, from which, by the aid of solvents, two substances were obtained in very small quantity. One of these did not melt at 300°; it behaved as an acid, and gave an unstable *silver* salt. The other substance crystallised in stellate clusters of needles, m. p. 228° (decomp.), had the composition $C_6H_3O_2NCl_2$, and the reactions of an aldehyde. It reduced ammoniacal silver solution, gave a white *substance* with ammonia, yielded a *p-nitrophenylhydrazone*, m. p. 237°, and formed a naphthacinchoninic *derivative*, m. p. 265°, with pyruvic acid and β-naphthylamine. For these reasons the substance is assigned the structure of 3 : 4-*dichloro*-2 : 5-*diaildehydopyrrole*,

$$\begin{matrix} CCl{:}C(CHO) \\ | \\ CCl{:}C(CHO) \end{matrix}\!\!>\!NH,$$

whilst the acid above-mentioned is probably the corresponding dibasic acid, 3 : 4-*dichloropyrrole*-2 : 5-*dicarboxylic acid*. R. V. S.

The Ferriammines. Giuseppe A. Barbieri and G. Pampanini (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 591–594).—Ferric thiocyanate yields with certain organic bases crystalline compounds containing for every molecule of thiocyanate three molecules of the base. They have a constitution similar to that of the tripyridinechromium chloride of Pfeiffer (Abstr., 1907, i, 872). *Tripyridineferric thiocyanate*, $Fe\begin{matrix}(SCN)_3\\(C_5NH_5)_3\end{matrix}$, is prepared by mixing the calculated quantities of ferric thiocyanate and pyridine in aqueous or, better, in ethereal solution. It forms dark green crystals, which are insoluble in water, but are soluble in various organic solvents with production of either red or violet solutions. *Triquinolineferric thiocyanate*, $Fe(SCN)_3(C_9H_7N)_3$, is similar to the pyridine derivative; it forms crystals which are almost black. *Triantipyrineferric thiocyanate*, $Fe(SCN)_3(C_{11}H_{12}ON_2)_3$, forms red crystals. R. V. S.

Rupture of the Pyridine Ring. Fritz Reitenstein and Wilhelm Breuning (*J. pr. Chem.*, 1911, [ii], 83, 97–130).—Zongerichten (Abstr., 1900, i, 51; compare Spiegel, *ibid.*, 1901, i, 752) has shown that 1-chloro-2 : 4-dinitrobenzene and pyridine form an additive compound containing a quinquevalent nitrogen atom, and Zincke (Abstr., 1904, i, 448, 921; 1905, i, 241, 923) has proved that this additive compound reacts with primary and secondary arylamines, yielding 2 : 4-dinitroaniline and derivatives of glutaconaldehyde of the type NHPhCl:CH·CH:CH·CH:CH·NHPh, due to the rupture of the pyridine ring (compare Dieckmann, Abstr., 1905, i, 411). It is now shown that other substances containing negative groups can form quaternary ammonium salts with pyridine, for example, diarylhaliminochlorides, benzanilideimidechloride, phosphorus pentachloride, etc., and that these additive compounds react with primary arylamines, producing a rupture of the pyridine ring and the formation of red dyes of the same type as those described by Zincke. It has

not been found possible to isolate definite additive compounds in all the cases studied, but the subsequent formation of a red dye by the action of an amine is regarded as proof of the formation of an additive compound between the pyridine and the compound containing the negative groups.

Di-o-tolyloxaliminochloride-pyridinium chloride,

$$C_5NH_5Cl\cdot C(:N\cdot C_6H_4Me)\cdot CCl:N\cdot C_6H_4Me,$$

obtained by warming a mixture of anhydrous pyridine and di-o-tolyloxalimino chloride (Bauer, Abstr., 1907, i, 603) with toluene, extracting the crude product with hot acetone, and crystallising the residue three times from methyl alcohol, forms intensely yellow-coloured plates, m. p. 180°. When boiled with water, acids, or alkalis, it is decomposed, and yields carbylamine derivatives. Its solution in concentrated sulphuric acid has a blood-red colour, and when poured into water yields oxalyl-o-toluidide. The *platinichloride*,

$$2C_{21}H_{19}N_3Cl_2,H_2PtCl_6,$$

forms orange-yellow crystals decomposing at 210—212°.

Diphenyloxaliminochloride-pyridinium chloride,

$$C_5NH_5Cl\cdot C(:NPh)\cdot CCl:NPh,$$

prepared in a similar manner from pyridine and diphenyloxalimino chloride, crystallises from methyl alcohol in yellow plates, which turn brown at 200° and melt at 203°.

When the di-o-tolyl derivative is warmed for a short time with an alcoholic solution of *p*-toluidine, Zincke's glutacondi-*p*-toluidide hydrochloride is obtained, and with an alcoholic solution of *β*-naphthylamine the corresponding *β*-naphthalide. The additive compound of pyridine and bezanilidedi-imidechloride (Wallach, this Journ., 1877, ii, 187) could not be isolated, but by the action of aniline, Zincke's dianilide was obtained, together with anilinobenzylideneaniline (Bernthsen, *Annalen*, 1877, **184**, 353).

A mixture of carbodiphenylimide (Schall, Abstr., 1895, i, 42), pyridine hydrochloride, and *p*-toluidine yields Zincke's *p*-toluidide, and a mixture of phosphorus pentachloride, pyridine, and aniline gives the corresponding anilide.

Pyridine dibromide and potassium cyanide react, yielding the product obtained by König from pyridine cyanogen bromide, and this with aniline yields the glutacondianilide. For the preparation of the anilide it is not necessary to isolate the intermediate compound.

Experiments on the chlorination of pyridine have been carried out. By chlorinating in dry ethereal solution, an unstable, colourless derivative is formed, which readily loses chlorine and reacts explosively with ether, alcohol, or aniline. With water, it yields dichloropyridine hydrochloride, $C_5NH_3Cl_2,HCl,H_2O$, which turns brown at 160° and melts at 168° (decomp.).

The product of chlorination yields a precipitate with mercuric chloride solution, and when this precipitate is decomposed by boiling with concentrated potassium chloride solution, dichloropyridine distils over, and this forms a *mercurichloride*, $C_5NH_5Cl_4Hg_2$, which crystallises from methyl alcohol in brilliant, colourless needles, m. p. 190°.

When pyridine is chlorinated without the addition of a solvent, but in the presence of zinc chloride or sea-sand, and at low temperatures,

a white precipitate is first obtained, but this re-dissolves, and ultimately a dark brown, viscous product is formed. The behaviour of the various chlorinated products towards primary amines has been studied. The white precipitate obtained by chlorinating pyridine in dry ethereal solution when distilled under reduced pressure gave fractions which did not yield dyes with primary arylamines. Similarly, the distillates obtained from the dark viscous liquid, formed by chlorinating pyridine in the presence of zinc chloride, did not give colorations with β-naphthylamine, neither did tri-, tetra-, and penta-chloropyridines. On the other hand, the white precipitate when left in contact with ether and the air underwent partial decomposition, and then reacted with aromatic bases, yielding red dyes of varying composition, and the undistilled dark viscid oil gave a red product with *p*-toluidine melting at 197—198°, with β-naphthylamine a *compound*, $C_{35}H_{27}N_3$, in the form of strongly electrical, dark red needles, m. p. 245°, and with α-methyldihydroindole a product in the form of a cochineal-red precipitate, which has not been analysed.

The *cis*- and *trans*-tolane dichlorides and phosphorus trichloride do not yield dyes with mixtures of pyridine and an aromatic amine.

A list of the various amines which react with the chlorinated pyridine is given, together with the colours produced. The characteristic line in the spectra of the various coloured condensation products is also given.

J. J. S.

Condensation Product of Ethyl Phthaliminoisobutyrylmalonate. SIEGMUND GABRIEL (*Ber.*, 1911, 44, 70—91. Compare this vol., i, 212).—The yellow by-product obtained by the interaction of ethyl sodiomalonate and α-phthaliminoisobutyryl chloride in benzene becomes the main product when $1\frac{1}{2}$ mols. of ethyl sodiomalonate are employed. (In the former method of preparation [*loc. cit.*] the yellow by-product is mixed with a colourless *substance*, m. p. 168—168·5°, which is shown to be *α-phthaliminoisobutyric anhydride* by its formation also from α-phthaliminoisobutyric acid and its chloride at 170°.) The same *substance*, $C_{16}H_{15}O_4N$, yellow prisms, m. p. 176—177°, is produced when ethyl α-phthaliminoisobutyrylmalonate is boiled with sodium in benzene. It no longer yields phthalic acid by hydrolysis with hydrochloric acid, and its behaviour, described below, points to the constitution of an ethyl benzoylenedimethylpyrrolonecarboxylate (I), obtained in accordance with the equation:

$$C_6H_4{<}{}^{CO}_{CO}{>}N\cdot CMe_2\cdot CO\cdot CH(CO_2Et)_2 =$$

$$\begin{matrix} C_6H_4\cdot C{:}C(CO_2Et) \\ | \qquad\ \ | \\ CO\text{---}N\cdot CMe_2\text{---} \end{matrix}{>}CO + CO_2 + C_2H_6O.$$

When the ester is hydrolysed by equal volumes of water and concentrated sulphuric acid, it yields *3-keto-2 : 2-dimethyl-2 : 3-dihydropyrrole-5-o-benzoic acid*, $\begin{matrix} CMe_2\cdot NH \\ | \qquad \\ CO\text{---}CH \end{matrix}{>}C\cdot C_6H_4\cdot CO_2H$ (II) [*hydrobromide*, $C_{13}H_{13}O_3N,HBr,H_2O$, m. p. 200° (decomp.)], which readily suffers ring closure at its m. p., 191° (decomp., rapidly heated), or by prolonged boiling

with mineral acids, yielding *benzoylenedimethylpyrrolone* (III), $\begin{matrix}C_6H_4\cdot C{=}CH\\ CO{-}N\cdot CMe_2\end{matrix}\!>\!CO$, m. p. 125—126°. This is reconverted into (II) by warm alkalis, and forms *benzoylene-4-bromodimethylpyrrolone* (IV), $\begin{matrix}C_6H_4\cdot C{=}CBr\\ CO{-}N\cdot CMe_2\end{matrix}\!>\!CO$, m. p. 224—225°, with bromine in glacial acetic acid. Substance (III) is reduced by hydriodic acid and red phosphorus to *benzoylene-dimethylpyrrolidone* (VII), $\begin{matrix}C_6H_4\cdot CH\cdot CH_2\\ CO{-}N{=}CMe_2\end{matrix}\!>\!CO$, m. p. 172—173°, which is also formed from (I) and from (II) by the same reducing agent. Substance (VII), unlike (III), is not ruptured by warm alkalis, forms a *phenylhydrazone*, m. p. 215—217·5°, and an *oxime*, 220—221·5°, and yields a *nitro*-compound, $C_{13}H_{12}O_4N_2$, m. p. 172—173° (decomp.), with warm fuming nitric acid.

When substance (III) is treated with fuming nitric acid below 20°, it is converted into *benzoylene-4-nitrodimethylpyrrolone* (V), $\begin{matrix}C_6H_4\cdot C{:}C(NO_2)\\ CO{-}N{-}CMe_2\end{matrix}\!>\!CO$, m. p. 264—265° (decomp.), which is reduced by hydriodic and glacial acetic acids, partly to substance (VII), partly to *benzoylene-4-amino-dimethylpyrrolone* (VI), $C_{13}H_{12}O_2N_2$, orange-red prisms, m. p. 212°.

By treatment with methyl-alcoholic hydrogen chloride, substance (II) yields the *hydrochloride*, m. p. 199—199·5° (decomp.), of its methyl ester, an aqueous solution of which is reconverted into (II) by an excess of sodium carbonate. Bromine in glacial acetic acid converts (II) into *4-bromo-3-keto-2 : 2-dimethyl-2 : 3-dihydropyrrole-5-o-benzoic acid* (VIII), $CO_2H\cdot C_6H_4\cdot C\!<\!\begin{matrix}CBr\cdot CO\\ NH\cdot CMe_2\end{matrix}$, m. p. 223° (slowly heated), which is re-converted into (II) and another (unexamined) substance by 20% potassium hydroxide on the water-bath; is almost unattacked by aniline at 150° (substance IV is produced in this experiment), and reacts with alcoholic ammonia at 100° to form a *substance*, $C_{13}H_{12}O_2N_2$ (XI), m. p. 303—304°, and with methylamine to form a *substance*, $C_{13}H_{11}MeO_2N_2$ (XIII), m. p. 222—223°, the constitutions of which are discussed below.

By the action of cold hydrochloric acid and potassium nitrite, substance (II) is changed into *1 : 4-dinitroso-3-keto-2 : 2-dimethyl-2 : 3-dihydropyrrole-5-o-benzoic acid* (IX), $CO_2H\cdot C_6H_4\cdot C\!<\!\begin{matrix}C(NO)\cdot CO\\ N(NO)\cdot CMe_2\end{matrix}$, m. p. about 160° (decomp.), which is converted by warm aqueous sodium carbonate into *4-nitroso-3-keto-2 : 2-dimethyl-2 : 3-dihydropyrrole-5-o-benzoic acid* (X), $CO_2H\cdot C_6H_4\cdot C\!<\!\begin{matrix}C(NO)\cdot CO\\ NH{-}{-}CMe_2\end{matrix}$, m. p. 182° (decomp.). This substance (X), which is obtained more conveniently by treating (II) with 50% alcohol, 50% acetic acid, and potassium nitrite, forms a *silver* salt, $C_{13}H_{11}O_4N_2Ag,H_2O$, decomp. 260—270°, and is

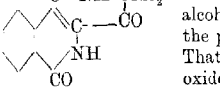
regarded as containing the nitroso-group in position 4 for the following reasons. It yields substance (VIII) with alcoholic bromine, is converted by nitric acid, D 1·2, into the *4-nitro-acid* (X*a*),

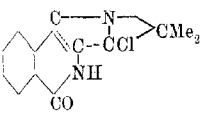
$$CO_2H\cdot C_6H_4\cdot C\ll\begin{matrix}C(NO_2)\cdot CO\\ |\\ NH\text{---}CMe_2\end{matrix},$$

m. p. 262—264° (decomp) (which is changed into V by boiling acetic anhydride), and is reduced, as also is (X*a*), by hydriodic and glacial acetic acids to substance (XI). This substance forms yellow crystals, gives a bluish-green fluorescent solution in boiling water, and a malachite-green solution in concentrated sulphuric acid, from which a blue powder is precipitated by the addition of water. Its insolubility in aqueous ammonia proves the absence of a carboxyl group, and its formation from substances (VIII) and (X) is explained by the formation of the same (unisolated) intermediate compound,

$$CO_2H\cdot C_6H_4\cdot C\ll\begin{matrix}NH\text{---}CMe_2\\ |\\ C(NH_2)\cdot CO\end{matrix},$$

from which substance (XI) (annexed constitution) is obtained by the elimination of water. The substance, which is called *gyrolone*, is isomeric with substance (VI); in fact, (VI) can be converted into gyrolone by the action of alcoholic potassium hydroxide and treatment of the product with aqueous ammonium chloride. That the solubility of gyrolone in alkali hydroxides is due to the presence of the acidic imino-group is indicated by the fact that substance (XIII), which contains NMe, is insoluble in these solvents; (XI) is converted into (XIII) by methyl-alcoholic potassium hydroxide and methyl iodide. By treatment with phosphoryl chloride on the water-bath, gyrolone is converted into a *substance*, $C_{13}H_{11}ON_2Cl$, pale yellow needles, which sublimes under diminished pressure, has m. p. 196°, develops a malachite-green coloration in concentrated sulphuric acid, is insoluble in aqueous ammonia, but dissolves in alkali hydroxides; these properties point to the annexed constitution. The substance, which is called *chlorogyrilone*, is converted by methylation into the same *N-methyl* homologue,





$C_{14}H_{10}MeON_2Cl$,

m. p. 128—128·5°, as is obtained by the action of phosphoryl chloride on substance (XIII).

By reduction with hydriodic acid, b. p. 127°, and red phosphorus, chlorogyrilone is converted into a *base*, $C_{13}H_{10}O_2N_2$, citron-yellow needles, m. p. 196—198°, which loses H_2O in a vacuum, yielding *dihydrogyrilone*, $C_6H_4\ll\begin{matrix}C\cdot NH\\ ||\\ CO\cdot NH\cdot C\cdot CH_2\end{matrix}\gg CMe_2$, m. p. 190—198°, clarifying completely at 210°, a solution of which in dilute sulphuric acid reduces gold and silver salts and also Fehling's solution. The product of the oxidation, $C_{13}H_{12}ON_2$, m. p. 212° (decomp.) (the *hydrochloride*, *chromate*, *aurichloride*, and *platinichloride* are mentioned), is obtained best by oxidising a solution of dihydrogyrilone or of its hydrate in

hydrochloric acid with an excess of bromine; the substance probably has the constitution $C_6H_4<\begin{matrix}C\cdot N\\ \\ CO\cdot NH\cdot C\cdot CH\end{matrix}>CMe_2$.

When a solution of gyrilone in fuming hydrochloric acid is heated at 135° for two hours and the resulting green powder is distilled in a vacuum, a *substance*, $C_{15}H_{12}ON_2$, isomeric with gyrilone, but devoid of basic properties, is obtained. It crystallises in yellow leaflets, melts and decomposes above 300°, and sublimes when heated carefully on a watch-glass; its constitution is as yet unascertained. C. S.

Transformation of Naphthalimide into Naphthastyril. Elie E. Pisovschi (*Bull. Soc. chim.*, 1911, [iv], 9, 86—88).—As the processes described by Francesconi and Recchi (Abstr., 1901, i, 721), and by Ullmann and Cassirer (Abstr., 1910, i, 201), do not give good yields, the following new process, which gives a quantitative yield, has been devised.

Naphthalimide (40 grams) dissolved in 600 c.c. of sodium hydroxide solution (3%) is treated at 40° with 480 c.c. of sodium hypochlorite solution containing 5·5% by weight of active chlorine, and the mixture warmed for thirty minutes at 65°. To this, 172 c.c. of sodium hydrogen sulphite solution (30%) are added, and the cooled mixture filtered and the filtrate diluted to 2750 c.c. From this, naphthastyril is precipitated in three fractions by (*a*) adding acetic acid, (*b*) adding dilute sulphuric acid, and (*c*) concentrating the mother liquors. The product may be crystallised from acetic acid.

Dilute solutions of naphthastyril in organic solvents show a green fluorescence. The solution in sulphuric acid is yellow (compare Ekstrand, Abstr., 1886, 715; 1889, 52). T. A. H.

Diacetyl. Diacetylmonophenylhydrazones and their Condensations. Otto Diels and Anton Kollisch (*Ber.*, 1911, 44, 263—268. Compare Abstr., 1903, i, 400; 1905, i, 509; 1907, i, 480; 1909, i, 455).—Although diacetylphenylhydrazone is not decomposed when boiled with hydrochloric acid, the corresponding phenylmethylhydrazone is readily transformed into 1-acetyl-2-methylindole when well shaken with warm hydrochloric acid. The phenylhydrazone and the phenylmethylhydrazone condense readily with ethyl oxalate, yielding hydrazones of ethyl diacetyloxalate, but so far it has not been found possible to remove the hydrazo-group from the condensation products.

Diacetylphenylmethylhydrazone, $COMe\cdot CMe{:}N\cdot NMePh$, is formed, together with a small amount of the corresponding osazone, by the action of phenylmethylhydrazine on diacetyl in acetic acid solution. It is a deep yellow oil, has b. p. 154—155°/14 mm. (corr.) and D^{20} 1·0809, and condenses with ethyl oxalate in the presence of dry sodium ethoxide and anhydrous ether, yielding the *phenylmethylhydrazone* of *ethyl diacetyloxalate*,

$$CO_2Et\cdot CO\cdot CH_2\cdot CO\cdot CMe{:}N\cdot NMePh,$$

which crystallises from methyl alcohol in red needles, m. p. 88° after

sintering. The corresponding *phenylhydrazone*, $C_{14}H_{16}O_4N_2$, crystallises from alcohol in golden-yellow plates, m. p. 148—149° (corr.).

1-*Acetyl*-2-*methylindole*, $C_6H_4<^{CH}_{NMe}>CAc$, crystallises from light petroleum in stout, colourless plates, m. p. 72°, and yields a *picrate*, $C_{17}H_{14}O_8N_4$, in the form of long, orange needles, m. p. 117°, and a *phenylhydrazone*, $C_{17}H_{17}N_3$, in the form of long, nearly colourless, needles, m. p. 117—118°. J. J. S.

Isatinanils. IV. Cases of Desmotropism. Rudolf Pummerer [with F. Grube] (*Ber.*, 1911, **44**, 338—345. Compare Abstr., 1910, i, 511).—Isatin-2-anil crystallises from benzene in brownish-violet prisms, m. p. 126°, but is precipitated by sodium carbonate from solutions of its salts in brown, crystalline flakes, which crystallise from dilute alcohol in large, yellowish-brown plates, m. p. 126°. At about 110°, partial transference into the violet form is observed. The two modifications are not identical, the yellow leaflets representing isatin-2-anil, $C_6H_4<^{NH}_{CO}>C{:}NPh$, and the violet prisms, isatin-2-anilide, $C_6H_4<^{N}_{CO}>C{\cdot}NHPh$. The violet form immediately gives red solutions; the yellow form yields yellowish-brown solutions in anhydrous solvents at low temperatures, which soon become red.

1-*Methylisatin*-2-*anil*, $C_6H_4<^{NMe}_{CO}>C{:}NPh$, is obtained by the action of sodium methoxide and methyl iodide; it crystallises in yellowish-red prisms, m. p. 132°, and is hydrolysed by acids to 1-methylisatin and aniline.

Isatin-2-*methylanilide*, $C_6H_4<^{N}_{CO}>C{\cdot}NMePh$, prepared by the interaction of isatin chloride with methylaniline in benzene solution, crystallises in long, bluish-violet plates, m. p. 103—104°. It is hydrolysed into isatin and methylaniline.

In the case of both isomerides the introduction of methyl causes a deepening of the colour. There is a considerable difference in the basicity of the two forms; the methyl-anil does not react with concentrated sodium hydrogen sulphite solution, whereas the methylanilide forms almost quantitatively a sparingly soluble bisulphite compound.

A similar isomerism has been studied in the case of thioindigoscarlet-2-anil, which is red, and thioindigoscarletanilide, which is greenish-brown (compare following abstract). In this example the anil form is more stable, and has been studied in solution. It is best converted into the anilide by means of acids, boiling with pyridine being the most satisfactory method of effecting the reverse change. E. F. A.

Indirubinanils: Substances with Reactive Carbon Double Bonds. Rudolf Pummerer [with Maximilian Goettler] (*Ber.*, 1911, **44**, 346—356. Compare preceding abstract; also Abstr., 1910, i, 511). —Isatin-2-anil reacts in alkaline solution with indoxyl, forming

indirubin-2-anil, in which the anil residue, being no longer in the neighbourhood of a CO group, is firmly fixed. In a similar manner indirubin-*p*-dimethylamino-2-anil and the corresponding sulphur compound have been prepared: both are blue dyes.

Thioindigo-scarlet-*p*-dimethylamino-2-anil on prolonged heating with 1% hydrogen chloride is decomposed quantitatively into aminodimethylaniline and thioindigo-scarlet, but the indirubin compound under similar treament only gives small quantities of indirubin, the main part being converted into a reddish-brown compound, $C_{15}H_{11}O_2N$, which has not been further investigated.

Indirubin-2-anil is decomposed by indoxyl into an indigo dye and *oxindoleanil*, $C_6H_4<^{CH_2}_{NH}>C{:}NPh$. The reaction is quantitative, and takes place rapidly in hot dilute acetic acid.

The carbon double bond in indirubinanil is opened by the action of phenylhydrazine, and isatin-2-phenylhydrazone is formed.

Oxidoleanil forms colourless flakes, m. p. 90—92°; it rapidly becomes violet on exposure to moist air. The *hydrochloride* forms short, lancet-shaped crystals, m. p. 219—220°. When warmed with nitrosobenzene, isatindianil is formed.

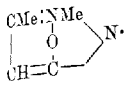
The brown modification of *thioindigo-scarlet-2-anilide* [*3(1′)-thionaphthenyl-ψ-indole-2-anilide*], $C_6H_4<^{S}_{CO}>C{:}C<^{C_6H_4}_{C(NHPh)}>N$ (see preceding abstract), formed by the interaction of isatin-2-anil with 2-hydroxythionaphthen, crystallises in long, narrow, brown prisms, m. p. 226—227°. The red *anil* form, $C_6H_4<^{S}_{CO}>C{:}C<^{C_6H_4}_{C(:NPh)}>NH$, prepared by boiling the brown form in dry pyridine, crystallises in carmine-red prisms with a coppery lustre.

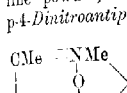
3(1′)-Thionaphthenyl-ψ-indole-p-*dimethylamino-2-anil* crystallises in lustrous, violet-black plates, m. p. 220—221°.

Indirubin-p-*dimethylamino-2-anil* forms bluish-violet plates, m. p. 257—258°. The *sulphate* forms rectangular violet-black plates of metallic lustre, m. p. 255—256°. E. F. A.

1-Nitro- and 1-Amino-derivatives of Antipyrine, Thiopyrine, and Anilopyrine. August Michaelis [with Walter Graff, Richard Gesing, and Heinrich Boie] (*Annalen*, 1911, 378, 293—351).—A previous attempt to prepare *p*-nitroantipyrine from methyl iodide and 5-chloro-1-*p*-nitrophenyl-3-methylpyrazole failed, because the two reagents yielded an iodo-*p*-nitrophenylmethylpyrazole methiodide, from which the *p*-nitroantipyrine could not be obtained by the action of alkalis or of silver oxide (Michaelis and Behn, Abstr., 1900, i, 693). Success has now been attained by treating the chloro-*p*-nitrophenylmethylpyrazole with an excess of methyl sulphate at 110° and treating the neutralised aqueous solution of the methosulphate with potassium iodide, whereby *5-chloro-1-p-nitrophenyl-3-methylpyrazole methiodide*, $^{CH\text{———}CMe}_{CCl\cdot N(C_6H_4\cdot NO_2)}>N,MeI$, yellow crystals, m. p. 196°, is obtained; an aqueous solution of this methiodide, by treatment with

silver oxide and subsequent evaporation, yields p-*nitroantipyrine* (1-p-*nitrophenyl*-2 : 3-*dimethyl*-5-*pyrazolone*) (annexed formula), yellow prisms, m. p. 132°. *p*-Nitroantipyrine, which can also be prepared, although less satisfactorily, by warming an aqueous solution of the preceding methiodide with the calculated quantity of hydroxylamine hydrochloride and sodium carbonate, forms a *hydrochloride*, $C_{11}H_{11}O_3N_3,HCl$, m. p. 191·5°, which is decomposed by water; *platinichloride*, large, red crystals; *hydriodide*, m. p. 165° (decomp.), and *picrate*, m. p. 101°. The methine hydrogen atom in position 4 exhibits its customary activity. Thus, by treatment with sodium nitrite in glacial acetic acid, *p*-nitroantipyrine yields p-*nitro*-4-*nitrosoantipyrine*, a green, crystalline powder, which becomes yellow at 176° and has m. p. 188—189°. p-4-*Dinitroantipyrine* (annexed formula), colourless needles, m. p. 276°, is prepared by the action of nitric and sulphuric acids on antipyrine, by treating *p*-nitroantipyrine with nitric acid, or by heating 5-*chloro*-4-*nitro*-1-p-*nitrophenyl*-3-*methylpyrazole*, m. p. 181° (obtained by the action of nitric and sulphuric acids on 5-chloro-1-phenyl-3-methylpyrazole) with methyl sulphate at 115—120° and decomposing the resulting methosulphate with sodium carbonate.

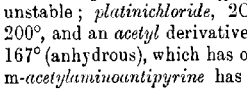




4-*Bromo*-p-*nitroantipyrine*, obtained from the nitroantipyrine and bromine in chloroform solution, has m. p. 173°. By reduction with tin and hydrochloric acid, *p*-nitroantipyrine yields *p*-aminoantipyrine, m. p. 210°, which does not condense with aldehydes; its *hydrochloride*, $C_{11}H_{13}ON_3,2HCl$, has m. p. 220° (decomp.). The *acetyl* derivative, m. p. 221°, forms 4-*nitroso* p-*acetylaminoantipyrine*, green needles, m. p. 237° (decomp.), with potassium nitrite in acetic acid solution, and 4-*bromo*-p-*acetylaminoantipyrine*, m. p. 240°, with bromine in chloroform. p-*Benzoylaminoantipyrine*, m. p. 261°, yields 4-*nitroso*-p-*benzoylaminoantipyrine*, m. p. 214°, and 4-*bromo*-p-*benzoylaminoantipyrine*, m. p. 237°, by similar processes. p-*Benzenesulphonylaminoantipyrine*, m. p. 251°, obtained from *p*-aminoantipyrine and benzenesulphonyl chloride in alcoholic solution, yields a 4-*nitroso*-compound, m. p. 211° (decomp.), and a 4-*bromo*-compound, m. p. 235°. p-4-*Diaminoantipyrine*, m. p. 279°, obtained by reducing dinitroantipyrine by tin and hydrochloric acid, forms a *diacetyl* derivative, m. p. 291°, which has only a slight antipyretic action.

The following compounds of *m*-nitroantipyrine and of *o*-nitroantipyrine are obtained, in the main, by processes similar to those mentioned above. 5-*Chloro*-1-m-*nitrophenyl*-3-*methylpyrazole methiodide*, m. p. 222°, yellow needles. m-*Nitroantipyrine*, m. p. 98°, yellow needles, forms a *hydrochloride*, m. p. 188°, which is decomposed by water; *platinichloride*, $2C_{11}H_{11}O_3N_3,H_2PtCl_6,2H_2O$, m. p. 140°; *hydriodide*, m. p. 171°; *picrate*, m. p. 165°, and *nitrate*, m. p. 143°. m-*Nitro*-4-*nitrosoantipyrine*, green crystals, decomp. 165°, complete at 188—190°. m-4-*Dinitroantipyrine*, prepared from *m*-nitroantipyrine and nitric acid with cooling, decomposes at 203°. 4-*Bromo*-m-*nitro*-

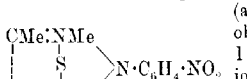
antipyrine, m. p. 184°. m-*Aminoantipyrine*, m. p. 148°, does not react with aldehydes, phenylthiocarbimide, or carbon disulphide; it forms a *hydrochloride*, $C_{11}H_{13}ON_3,2HCl$, m. p. 228°, which is very unstable; *platinichloride*, $2C_{11}H_{13}ON_3,H_2PtCl_6,2H_2O$, decomp. above 200°, and an *acetyl* derivative, $C_{13}H_{15}O_2N_3,H_2O$, m. p. 127° (hydrated), 167° (anhydrous), which has only a slight antipyretic action. 4-*Bromo*-m-*acetylaminoantipyrine* has m. p. 217°. m-*Benzoylaminoantipyrine* has m. p. 119°. m-*Dimethylaminoantipyrine* (*ψ-pyramidone*) (annexed formula), obtained by heating *m*-aminoantipyrine and methyl sulphate nearly at the b. p. for half an hour and basifying the aqueous solution of the resulting methosulphate, is an oil which forms a *platinichloride*, reddish-brown needles, m. p. 270° (decomp.).



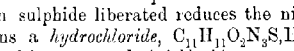
m-4-*Diaminoantipyrine*, m. p. 170°, forms a *hydrochloride*, $C_{11}H_{14}ON_4,2HCl$, m. p. 245°, and a *diacetyl* derivative, m. p. 273°.

5-*Chloro*-1-o-*nitrophenyl*-3-*methylpyrazole methiodide*, m. p. 183°, yellow prisms, is converted by silver oxide in the preceding manner into o-*nitroantipyrine*, m. p. 188°, which forms a *hydrochloride*, m. p. 201°, and *platinichloride*, $2C_{11}H_{11}O_2N_3,H_2PtCl_6,2H_2O$, m. p. 133° (hydrated), decomp. above 300° (anhydrous). o : 4-*Dinitroantipyrine*, white needles, has m. p. 244°. o-*Aminoantipyrine* has m. p. 165°.

2 : 5-*Thio*-1-m-*nitrophenyl*-2 : 3-*dimethylpyrazolone* (m-*nitrothiopyrine*) (annexed formula), m. p. 204°, yellow leaflets, obtained by treating a suspension of 5-chloro-1-*m*-nitrophenyl-3-methylpyrazole methiodide in chloroform with a concentrated alcoholic solution of potassium sulphide (the use of aqueous solutions is to be avoided, since the hydrogen sulphide liberated reduces the nitro-group to the amino-group), forms a *hydrochloride*, $C_{11}H_{11}O_2N_3S,HCl$, m. p. 147°, which is decomposed by water, *platinichloride*, m. p. 225°, *hydriodide*, m. p. 185°, *methiodide*, m. p. 209°, and *trioxide*, $C_{11}H_{11}O_5N_3S$, m. p. above 350°, the last being obtained by passing chlorine through a hot aqueous solution of the nitrothiopyrine.



5-*Methylthiol*-1-m-*nitrophenyl*-3-*methylpyrazole* (m-*nitro-ψ-thiopyrine*),



m. p. 84°, white needles, is obtained by carefully heating *m*-nitrothiopyrine methiodide under reduced pressure; by oxidation by potassium permanganate in glacial acetic acid, it yields the *sulphone*,

$$C_{11}H_{11}O_4N_3S,$$

m. p. 135°. m-*Aminothiopyrine*, m. p. 199°, obtained by reducing the nitrothiopyrine by tin and hydrochloric acid, forms a *hydrochloride*, m. p. 226°, and *platinichloride*, an amorphous, red powder. The following compounds are obtained by methods similar to the preceding: 2 : 5-*thio*-1-o-*nitrophenyl*-2 : 3-*dimethylpyrazolone* (o-*nitrothiopyrine*), m. p. 190°, blood-red crystals, forms a *hydrochloride*, m. p. 125°, *platinichloride*, decomp. 230°, *hydriodide*, m. p. 152°, *methiodide*, m. p. 181°, and *trioxide*, m. p. 298°. o-*Nitro-ψ-thiopyrine* and its sulphone have m. p. 61° and 160° respectively. o-*Aminothiopyrine*,

m. p. 172°, forms a *platinichloride*, decomp. 300°. 2 : 5-*Thio*-1-p-*nitrophenyl*-2 : 3-*dimethylpyrazolone* (p-*nitrothiopyrine*), m. p. 241°, red crystals, is obtained by treating a hot aqueous solution of 5-chloro-1-*p*-nitrophenyl-3-methylpyrazole methiodide with concentrated aqueous sodium sulphide; it forms a *hydrochloride*, m. p. 175°, *methiodide*, m. p. 196°, and *trioxide*, decomp. above 370°. *p*-Nitro-ψ-thiopyrine (Michaelis and Besson, Abstr., 1904, i, 780) forms a *hydrochloride*, m. p. 85°, and a *sulphone*, m. p. 154°; 4-*bromo*-p-*nitro*-ψ-*thiopyrine* has m. p. 120°. p-4-*Dinitrothiopyrine*, m. p. 240°, yellow crystals, obtained in a similar manner to the dinitroantipyrine, forms a *methiodide*, m. p. 154—155°, which by heating under reduced pressure yields the *dinitro*-ψ-*thiopyrine*, m. p. 123°; the corresponding *sulphone* has m. p. 177°. p-*Aminothiopyrine*, m. p. 255—256°, obtained by the reduction of *p*-nitrothiopyrine, forms a *hydrochloride*, $C_{11}H_{13}N_3S,2HCl$, an *acetyl* derivative, m. p. 271°, and *benzoyl* derivative, m. p. 265°. p-*Amino*-ψ-*thiopyrine*, m. p. 132°, white leaflets, obtained by the reduction of *p*-nitro-ψ-thiopyrine, forms a *hydrochloride*, $C_{11}H_{13}N_3S,2HCl$, m. p. 221°, and an *acetyl* derivative, m. p. 137°. p-4-*Diaminothiopyrine*, m. p. 207°, obtained in a similar manner to the diaminoantipyrine, forms a *diacetyl* derivative, m. p. 273°. p-4-*Diamino*-ψ-*thiopyrine*, m. p. 115°, white needles, is obtained by the reduction of the dinitro-ψ-thiopyrine; its *diacetyl* derivative has m. p. 235°.

2 : 5-endo*Ani'o*-1-m-*nitrophenyl*-2 : 3-*dimethylpyrazole* (m-*nitroanilopyrine*) (annexed formula),

m. p. 110°, reddish-brown needles, is obtained by heating 5-chloro-1-*m*-nitrophenyl-3-methylpyrazole methiodide and aniline (2 mols.) at 125° for two hours. It reduces Fehling's solution and silver salts, and is a strong base; the *hydriodide*, m. p. 166°, *platinichloride*, *picrate*, *thiocyanate*, m. p. 168°, *methiodide*, m. p. 222°, *ethiodide*, m. p. 176°, and *propiodide*, m. p. 130°, are described. By treatment with benzoyl chloride in benzene, *m*-nitroanilopyrine forms a *benzoyl chloride*, which is isolated as the *platinichloride*, $2(C_{17}H_{15}O_2N_4C_6H_5{\cdot}COCl)PtCl_4$, m. p. 235°; from this, by aqueous potassium iodide, the *benzoyliodide*, m. p. 198°, is obtained; the *acetyliodide*, $C_{17}H_{16}O_2N_4,CH_3{\cdot}COI$, has m. p. 214°. When heated at 200°, *m*-nitroanilopyrine hydrochloride loses methyl chloride, and is converted into 5-*anilino*-1-m-*nitrophenyl*-3-*methylpyrazole*, m. p. 122—123°, yellow needles.

2 : 5-endo*Anilo*-1-o-*nitrophenyl*-2 : 3-*dimethylpyrazole* (*o*-*nitroanilopyrine*), m. p. 111°, dark red prisms, is obtained in a similar manner to the meta-compound, using 4 mols. of aniline at 110°. It is likewise a strong base, forming a *platinichloride*, m. p. 206°, *hydriodide*, m. p. 198°, *picrate*, m. p. 167°, *thiocyanate*, m. p. 193°, *methiodide*, m. p. 97°, *ethiodide*, m. p. 177°, *propiodide*, m. p. 168°, *acetyliodide*, m. p. 225°, *benzoyliodide*, m. p. 197°, and *benzoyl chloride*, m. p. 124°; by heating the last at 50—80°/40 mm., 5-*benzoylanilino*-1-*o*-*nitrophenyl*-3-*methylpyrazole*, m. p. 156—157°, white prisms, is obtained. 1-*Azo*-*o*-*anilopyrine*, $N_2(C_6H_4{\cdot}C_3N_2Me_2{\cdot}NPh)_2$, red needles, m. p. 225°, is prepared by heating an alcoholic solution of *o*-nitroanilopyrine with aluminium amalgam and a little water on the water-bath.

2 : 5-endo*Anilo*-1-p-*nitrophenyl*-2 : 3-*dimethylpyrazole* (p-*nitroanilopyrine*), m. p. 168°, dark red crystals, is prepared by heating 5-chloro-1-*p*-nitrophenyl-3-methylpyrazole with methyl sulphate and treating the resulting methosulphate with aniline at 125—130° for five hours; the *hydriodide* has m. p. 192°, and the *methiodide*, m. p. 182°. By heating the latter at 200° under reduced pressure, p-*nitro-ψ-anilopyrine*, $\begin{matrix}CMe{:}N\\ \vert \\ CH{:}C(NPhMe)\end{matrix}\!\!>\!N\cdot C_6H_4\cdot NO_2$, m. p. 100°, yellow needles, is obtained. p : 4-*Dinitroanilopyrine*, m. p. 192°, yellow leaflets, is prepared by heating 5-chloro-4-nitro-1-*p*-nitrophenyl-3-methylpyrazole with methyl sulphate at 115—120° for six hours, and treating the resulting methosulphate with an excess of aniline at 130° for four hours. *p*-Nitroanilopyrine yields p-*aminoanilopyrine*, m. p. 175°, by reduction with tin and hydrochloric acid, and p-*azoanilopyrine*, m. p. 224°, dark red crystals, by reduction in alcohol-chloroform solution by aluminium amalgam and water. C. S.

Action of Diethylmalonyl Chloride on Some Substances Containing Nitrogen. Martin Freund and Karl Fleischer (*Annalen*, 1911, 379, 27—36. Compare Abstr., 1910, i, 490).—When warmed with acetamide (2 mols.), diethylmalonyl chloride yields 4 : 6-*diketo*-2-*methyl*-5 : 5-*diethyltetrahydropyrimidine hydrochloride*, $C_9H_{14}O_2N_2,HCl$, decomp. 253°, white needles, from which dilute aqueous ammonia liberates the *base* itself, $CEt_2\!<\!\begin{matrix}CO\text{—}N\\ CO\cdot NH\end{matrix}\!>\!CMe$, m. p. 125°. The constitution follows from the ready decomposition of the base into diethylmalonamide by warm alkalis. It separates from methyl alcohol in long needles, $C_9H_{14}O_2N_2,MeOH$, m. p. 135—140°, which at 100—110° lose methyl alcohol and are converted into a vitreous, yellow mass, which has pronounced acidic properties, and is probably the enolic form of the base, since it is converted by 20% hydrochloric acid into the preceding hydrochloride. Formamide and propionamide do not form pyrimidines with diethylmalonyl chloride.

By the prolonged interaction of benzamide and diethylmalonyl chloride with warming, diethylmalonamic acid, together with a little cyaphenine, are produced. By short, careful heating, however, the two substances yield *benzoyldiethylmalonamic acid*, $NHBz\cdot CO\cdot CEt_2\cdot CO_2H$, m. p. 127—128° (decomp.), together with *diethylacetylbenzamide*, $NHBz\cdot CO\cdot CHEt_2$, m. p. 138—139°, which is also formed by heating the preceding acid above its m. p.

When warmed with diethylmalonyl chloride, benzylidenesemicarbazone is converted into 3 : 5-*diketo*-1 : 2-*diethylmalonyl*-4 : 4-*diethylpyrazolidine*, $CEt_2\!<\!\begin{matrix}CO\cdot N\cdot CO\\ \vert \\ CO\cdot N\cdot CO\end{matrix}\!>\!CEt_2$, m. p. 202—203°. This is converted by warm dilute sodium hydroxide and subsequent acidification into *bisdiethylmalonhydrazinic acid*, $N_2H_2(CO\cdot CEt_2\cdot CO_2H)_2$, m. p. 233—234° (decomp.), which is very stable to alkalis and to sulphuric acid, but is converted by careful heating into *bis-α-ethylbutyrylhydrazide*, $N_2H_2\cdot CO\cdot CHEt_2$, m. p. 234°.

[With MAX ROTHSCHILD.]—Benzylidenesemicarbazone and dipropylmalonyl chloride yield the corresponding *3 : 5-diketo-1 : 2-dipropyl-carbonyl-4 : 4-dipropylpyrazolidine*, $C_{18}H_{28}O_4N_2$, m. p. 189°. C. S.

[Benzoylenecarbamide.] HERMANN FINGER and H. GÜNZLER (*J. pr. Chem.*, 1911, [ii], **83**, 198—199).—The substance designated as ethyl cyanoanilide-*o*-carboxylate (Finger and Zeh, Abstr., 1910, i, 382) has been described previously by Griess under the name ethoxycyanoaminobenzene (4-keto-2-ethoxy-1 : 4-dihydro-1 : 3-benzdiazine); he also mentions its conversion into benzoylenecarbamide. If this constitution is correct, the substance obtained from it by the action of methyl sulphate and described as *o*-carbethoxyphenylmethylcarbodi-imide (Finger, Abstr., 1910, i, 383) may very possibly be 4-keto-2-ethoxy-3-methyl-3 : 4-dihydro-1 : 3-benzdiazine,

$$C_6H_4\begin{cases} N{=}C(OEt) \\ | \\ CO\cdot NMe \end{cases}$$

C. S.

Condensation of Esters of Alkyloxy-acids with Cyanides and Ketones. REINHOLD VON WALTHER (*J. pr. Chem.*, 1911, [ii], **83**, 171—182).—[With H. LITTER.]—*Phenoxyacetylacetophenone*,

$$OPh\cdot CH_2\cdot CO\cdot CH_2\cdot COPh,$$

m. p. 79—80°, white needles, obtained by acidifying the product of the condensation of equimolecular quantities of ethyl phenoxyacetate and acetophenone in the presence of sodium ethoxide, gives a red coloration with alcoholic ferric chloride, does not react with phenylcarbimide or with benzoyl chloride and sodium hydroxide, but condenses with phenylhydrazine to form *1 : 3-diphenyl-5-phenoxymethylpyrazole*, $OPh\cdot CH_2\cdot C\begin{cases} CH{-}CPh \\ \| \\ NPh\cdot N \end{cases}$, m. p. 88°, which is reduced by sodium and alcohol to 1 : 3-diphenyl-5-methylpyrazoline, phenol being eliminated. *3-Phenyl-5-phenoxymethylpyrazole*, m. p. 104°, is obtained by boiling an alcoholic solution of phenoxyacetylacetophenone with aqueous hydrazine, whilst *3-phenyl-5-phenoxymethylisooxazole*, m. p. 61°, is produced in a similar manner with hydroxylamine hydrochloride.

[With P. HERSCHEL.]—*α-Phenoxyacetylphenylacetonitrile*,

$$OPh\cdot CH_2\cdot CO\cdot CHPh\cdot CN,$$

m. p. 125—126°, prepared from ethyl phenoxyacetate, phenylacetonitrile, and sodium ethoxide, dissolves in aqueous ammonia, and reacts with phenylhydrazine in boiling glacial acetic acid to form *5-imino-1 : 4-diphenyl-3-phenoxymethylpyrazolone*, $OPh\cdot CH_2\cdot C\begin{cases} N{-}{-}{-}NPh \\ | \\ CHPh\cdot C{:}NH \end{cases}$, m. p. 120—121°, the *hydrochloride*, *platinichloride*, m. p. 192° (decomp.), *picrate*, m. p. 163°, *benzoyl* derivative, m. p. 163—165°, and *acetyl* derivative, m. p. 174—175°, of which are described. Phenoxyacetyl phenylacetonitrile reacts with dry ammonia at 150° to form *β-amino-γ-phenoxy-α-phenylcrotononitrile*, $OPh\cdot CH_2\cdot C(NH_2){:}CPh\cdot CN$, m. p. 88—89°, and with aniline, *p*-toluidine, and α-naphthylamine to form corresponding *β*-anilino-, *β-p*-toluidino-, and *β*-naphthylamino-derivatives, m. p. 131°, 118°, and 145—150° respectively; also, by saturating

its solution in hot glacial acetic acid with hydrogen chloride it yields *γ-phenoxy-α-phenylacetoacetamide*, $OPh\cdot CH_2\cdot CO\cdot CHPh\cdot CO\cdot NH_2$, m. p. 151—152°, which reacts with hydroxylamine hydrochloride in boiling acetic acid to form *4-phenyl-3-phenoxymethylisooxazolone*,

$$OPh\cdot CH_2\cdot C\begin{array}{l}\diagup N\text{——}O\\ \diagdown CHPh\cdot CO\end{array}$$

m. p. 160—162° (decomp.), and with phenylhydrazine to form *2 : 4-diphenyl-3-phenoxymethylpyrazolone*, $OPh\cdot CH_2\cdot C\begin{array}{l}\diagup NPh\cdot NH\\ \diagdown CPh\cdot CO\end{array}$, m. p. 145°, a substance which is soluble in sodium hydroxide, carbonate, or hydrogen carbonate. Ethyl phenoxyacetate condenses with *p*-chlorophenylacetonitrile to form *p-chloro-α-phenoxyacetylphenylacetonitrile*,

$$OPh\cdot CH_2\cdot CO\cdot CH(C_6H_4Cl)\cdot CN,$$

m. p. 168°, from which the following substances are produced by reactions similar to the preceding: *5-imino-1-phenyl-4-p-chlorophenyl-3-phenoxymethylpyrazolone*, m. p. 107° (*hydrochloride*, *picrate*, m. p. 165°, *acetyl* derivative, m. p. 219°, *benzoyl* derivative, m. p. 219—220°); *β-amino-γ-phenoxy-α-p-chlorophenylcrotononitrile*, m. p. 132°; the corresponding *β-anilino-* and *β-p-toluidino*-derivatives have m. p. 122° and 135° respectively. *p*-Chloro-α-phenoxyacetylphenylacetonitrile, unlike the non-halogenated cyanide, reacts with hydroxylamine hydrochloride in boiling alcohol to form *5-imino-4-p-chlorophenyl-3-phenoxymethylisooxazolone*, $OPh\cdot CH_2\cdot C\begin{array}{l}\diagup CH(C_6H_4Cl)\cdot C:NH\\ \diagdown N\text{——}O\end{array}$, m. p. 108°.

Also, it does not form an amide, but with alcoholic hydrogen chloride yields *ethyl γ-phenoxy-α-p-chlorophenylacetoacetate*,

$$OPh\cdot CH_2\cdot CO\cdot CH(C_6H_4Cl)\cdot CO_2Et,$$

m. p. 70°; the *methyl* ester has m. p. 87°. With phenylhydrazine in boiling alcohol, the ester yields a *phenylhydrazide*,

$$OPh\cdot CH_2\cdot CO\cdot CH(C_6H_4Cl)\cdot CO\cdot NH\cdot NHPh,$$

m. p. 125—126°, which is easily converted by alcoholic sodium hydroxide into the *pyrazolone*, $OPh\cdot CH_2\cdot C\begin{array}{l}\diagup C(C_6H_4Cl)\cdot CO\\ \diagdown NPh\text{——}NH\end{array}$, m. p. 166°.

C. S.

Reaction Products of Potassium *iso*Cyanate and Diaminoacetone Hydrochloride. Amino- and Carbamido-propyleneureine [Carbamidomethylglyoxalone]. ANTOINE P. N. FRANCHIMONT and J. V. DUBSKY (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **13**, 625—628).—It is shown that when potassium *iso*cyanate and diaminoacetone hydrochloride interact, the products are not those described by Rügheimer (Abstr., 1892, ii, 952), but 4-carbamidomethylglyoxalone and aminopropyleneureine [4-aminomethylglyoxalone] hydrochloride.

Aminomethylglyoxaline hydrochloride, $\begin{array}{l}NH\cdot CH\\ CO\cdot NH\end{array}\!\!>C\cdot CH_2\cdot NH_2,HCl$, crystallises in small needles which are very soluble in water. The free base has not yet been isolated, but some of its compounds and derivatives are described. The *nitrate* and normal and acid *sulphates* all form small, colourless needles with no definite melting point. The

triacetyl derivative forms needles, m. p. 141°. The *tetra-acetyl* derivative, $\begin{matrix}NAc\cdot CH\\ |\\ CO\cdot NAc\end{matrix}\!\!>\!CH_2\cdot NAc_2$, crystallises in plates, m. p. 163—161°.

The *carboxymethyl* derivative forms leaflets, m. p. 238°, and when boiled with acetic anhydride yields a *monoacetyl* derivative,

$$C_3N_2H_3\cdot CH_2\cdot NHAc,$$

m. p. 215°. The *diacetyl* derivative crystallises in needles, m. p. 125—126°. The corresponding *carboxyethyl* derivative forms, small glittering crystals, m. p. 208°. It yields a *monoacetyl* compound, m. p. 218—219°, and a *diacetyl* compound, m. p. 101—102°.

4-Carbamidomethylglyoxalone, $\begin{matrix}NH\cdot CH\\ |\\ CO\cdot NH\end{matrix}\!\!>\!CH_2\cdot NH\cdot CO\cdot NH_2$, was obtained from diaminoacetone hydrochloride with 2 molecules of potassium *iso*cyanate, and also from aminomethylglyoxalone hydrochloride with 1 molecule of the *iso*cyanate. It forms snow-white leaflets, decomposing at 220°, and gives no precipitate with silver nitrate or mercuric chloride unless ammonia is added, but is precipitated by mercuric nitrate. N. C.

Phenanthrene Series. XXIX. Phenantriazines. Julius Schmidt, Otto Schairer, and Ernst Glatz (*Ber.*, 1911, **44**, 276—282. Compare Thiele and Bihan, Abstr., 1899, i, 47).—Hydroxyphenantriazine, $\begin{matrix}C_6H_4\cdot C:N\cdot CO\\ |\\ C_6H_4\cdot C:N\cdot NH\end{matrix}$ or $\begin{matrix}C_6H_4\cdot C:N\cdot C\cdot OH\\ ||\\ C_6H_4\cdot C:N\cdot N\end{matrix}$, is formed when phenanthraquinonemonoxime is boiled for ten hours with an alcoholic solution of semicarbazide hydrochloride, hydroxylamine being formed at the same time. Substituted derivatives of phenanthraquinonemonoxime react in much the same manner, and by using the 4-nitro-derivative it has been found possible to isolate the semicarbazone of the monoxime as an intermediate product. It has not been found possible to obtain the phenantriazine directly from phenanthraquinonemonosemicarbazone.

Phenanthraquinonesemicarbazone, $\begin{matrix}C_6H_4\cdot C:N\cdot NH\cdot CO\cdot NH_2\\ |\\ C_6H_4\cdot CO\end{matrix}$, crystallises from alcohol in golden, crystalline nodules or in long, brilliant golden-yellow needles containing 0·5 mol. of ethyl alcohol. Both forms have m. p. 220° (decomp.).

3-Hydroxyphenantriazine, $C_{15}H_9ON_3$, crystallises from alcohol in pale yellow nodules, m. p. 285° (decomp.), and does not give the usual reactions for ketones.

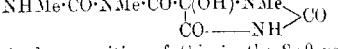
4-Nitrophenanthraquinonemonosemicarbazone, $C_{15}H_{10}O_4N_4$, forms a yellow, crystalline powder, m. p. 210—211° (decomp.).

4-Nitrophenanthraquinoneoximesemicarbazone, $C_{15}H_{11}O_4N_5$, forms a yellowish-green powder, m. p. 240° (decomp.), and yields *8-nitro-3-hydroxyphenantriazine*, $C_{15}H_8O_3N_4$, as a yellow powder, m. p. 285° (decomp.), when heated with alcohol and concentrated hydrochloric acid.

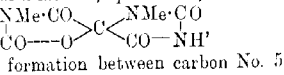
3-Bromophenanthraquinoneoximesemicarbazone form pale yellow, crystals, m. p. 274—275°, and *7-bromo-3-hydroxyphenantriazine* yellow crystals, m. p. 304°.

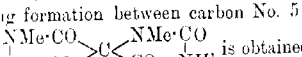
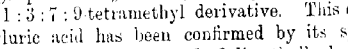
3-*Nitrophenanthraquinoneoximesemicarbazone* has m. p. 249—250° (decomp.), and *7-nitro-3-hydroxyphenantriazine* forms ochre-yellow crystals, m. p. 273—274° (decomp.). J. J. S.

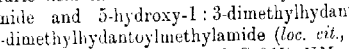
Hypocaffeine and its Decomposition. HEINRICH BILTZ and PAUL KREBS (*Ber.*, 1911, **44**, 282—305. Compare Abstr., 1910, i, 521, 524, 526).—The products described by Fischer (Abstr., 1882, 217; 1883, 356) under the names of hypocaffeine, caffoline, and acetcaffeine have been re-examined. The formula for hypocaffeine is shown to be $C_8H_{10}O_4N_4$, and not $C_6H_7O_3N_3$, as suggested by Fischer. A 60% yield of the compound is formed when trimethyluric-acid-glycol ether is decomposed by an alcoholic solution of hydrogen chloride in the absence of water; when aqueous hydrochloric acid is used, the yield is only 30%, and *apo*caffeine is also formed. The formulæ for the silver and barium salts are $C_8H_9O_4N_4Ag$ and $(C_8H_9O_4N_4)_2Ba$ respectively. When trimethyluric-acid-glycol ether is decomposed by concentrated sulphuric acid, *apo*caffeine and not hypocaffeine is formed. Caffoline has the formula $C_7H_{12}O_3N_4$, and in the conversion of hypocaffeine into caffoline by warming with barium carbonate solution a molecule of water is added and one of carbon dioxide eliminated, and the conversion of caffoline into acetcaffeine by boiling with acetic anhydride and hydrolysing the resulting acetyl derivative also consists in the addition of water and the removal of carbon dioxide and ammonia. These conclusions have been confirmed by molecular-weight determinations and the methylation of hypocaffeine to oxytetramethyluric acid (Fischer, Abstr., 1898, i, 180). In the conversion of the glycol ether into hypocaffeine, trimethyluric-acid-glycol is probably first formed: this is, however, unstable, and is ruptured at the 3 : 4 position, yielding 5-hydroxy-1-methylhydantoyl-7 : 9-dimethylcarbamide,



by the hydrolytic decomposition of this in the 8 : 9 position, and (*a*) subsequent formation of a lactone, *apo*caffeine,



is formed, or (*b*) ring formation between carbon No. 5 and nitrogen No. 9, hypocaffeine,  is obtained. According to Baeyer's nomenclature (*Ber.*, 1900, **33**, 3771), hypocaffeine is thus 1 : 7 : 9-*trimethyl*-spiro 5 : 5-*hydantoin*, and oxytetramethyluric acid, the corresponding 1 : 3 : 7 : 9-tetramethyl derivative. This constitution of oxytetramethyluric acid has been confirmed by its synthesis from dimethylcarbamide and 5-hydroxy-1 : 3-dimethylhydantoylamide or 5-hydroxy-1 : 3-dimethylhydantoylmethylamide (*loc. cit.*, p. 521) (*allo*-caffuric acid), 

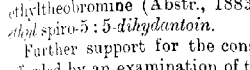


Hypocaffeine is not formed when methylcarbamide is fused with 5-hydroxy-1 : 3-dimethylhydantoylamide, or yet by heating dimethyl-

carbamide with caffuric acid alone or in presence of solvents, but can be synthesised together with oxytetramethyluric acid by heating dimethylcarbamide with 5-hydroxy-1-methylhydantoylmethylamide at 150° for eight to ten minutes whilst hydrogen chloride is passed through the mixture.

A *spiro*-dihydantoin is not formed by the decomposition of 7 : 9-dimethyluric-acid-glycol, as the rupture then occurs at the 8 : 9 position only. These facts are in perfect harmony with Biltz's views on the stability of the C·N union (*loc. cit.*, p. 324), when methyl is attached to the nitrogen. The formation of *spiro*-hydantoins is to be expected only when the uric acid is alkylated in position 3. Fischer's hypoethyltheobromine (Abstr., 1883, 357) is undoubtedly 1 : 9-*dimethyl*-7-*ethyl spiro*-5 : 5-*dihydantoin*.

Further support for the constitutional formula for hypocaffeine is afforded by an examination of the decomposition products of caffoline, namely, dimethylcarbamide or cholesterophan and methylcarbamide, from which it is argued that caffoline must be 1 : 3 : 6-*trimethylallantoin* (annexed formula), the formula of which is in harmony with most of the properties described by Fischer.



Caffoline and acetic anhydride yield acetylacecaffeine, carbon dioxide, and acetamide: $C_7H_{12}O_3N_4 + (CH_3\cdot CO)_2O = C_8H_{12}O_3N_4 + CO_2 + CH_3\cdot CO\cdot NH_2$, and the acetyl derivative when heated with concentrated hydrochloric acid yields acecaffeine hydrochloride, from which the free base is formed by the action of magnesium oxide and extracting the dry mass with benzene. The constitution 5-*methylamino*-1 : 3-*dimethylhydantoin*, $CO<^{NMe\cdot CO}_{NMe\cdot CH\cdot NHMe}$, is suggested for acecaffeine, and this agrees with its basic properties, with the readiness with which it can be oxidised to cholesterophan, and with the formation of methylamine, dimethylcarbamide, and glyoxylic acid on hydrolysis.

Caffoline can be synthesised by evaporating an aqueous solution of acecaffeine hydrochloride and potassium cyanate to dryness on the water-bath.

Free acecaffeine condenses readily with alkyl carbimides or thiocarbimides, yielding alkylated allantoins and thioallantoins, and this appears to be an extremely convenient method for the preparation of these types of compounds.

It is pointed out that the oxidation of uric acid and its monomethyl derivatives cannot be due to the intermediate formation of *spiro*-hydantoins, as, according to such a scheme, both 1-methyl and 9-methyluric acids should yield 3-methylallantoin, and the 3-methyl and 7-methyl acids should yield 1-methylallantoin, whereas Fischer and Ach (Abstr., 1900, i, 63) have shown that 3-methylallantoin is formed from the 1- and 7-methylated acids, and 1-methylallantoin from the 3- and 9-methylated acids.

Hypocaffeine has m. p. 185—186° (corr.), and 1 : 3 : 6-trimethylallantoin (caffoline), m. p. 197° (corr.). Hypocaffeine can also be obtained from 5-chloro 1 : 3 : 7-trimethyl*iso*uric acid (Abstr., 1911, i, 168) and the corresponding 5-alkyloxy-compounds, but this method

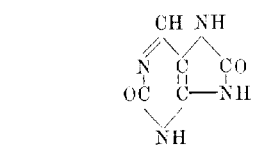
is not so convenient as Fischer's. In the alkylation of silver hypocaffeine by methyl iodide, the yield of oxytetramethyluric acid is only about 25—30%, and appreciable quantities of free hypocaffeine are formed. This is attributed to the conversion of a portion of the methyl iodide into hydrogen iodide and ethylene. When ethyl iodide is used, the silver compound is not alkylated. It has not been found possible to oxidise trimethyluric acid to a trimethylallantoin.

1 : 3 : 6 : 8-*Tetramethylallantoin*, $C_8H_{14}O_3N_4$, is readily formed when acecaffeine and methylcarbimide in benzene solution are sealed in a glass tube and left for twelve hours; it is also formed by the action of barium hydroxide solution on oxytetramethyluric acid. It absorbs water rapidly, yielding a monohydrate, which crystallises in rectangular prisms, m. p. 92°, after sintering at 85°. The anhydrous compound has m. p. 112—113°.

8-*Phenyl*-1 : 3 : 6-*trimethylallantoin*, $C_{13}H_{16}O_3N_4$, obtained from phenylcarbimide and acecaffeine in benzene solution and in the absence of moisture, crystallises from ethyl acetate, and has m. p. 197—198°. 7-*Thio*-1 : 3 : 6 : 8-*tetramethylallantoin*, $C_8H_{14}O_2N_4S$, crystallises from benzene in prisms, m. p. 158—159°. 7-*Thio*-1 : 3 : 6-*trimethyl*-8-*ethylallantoin*, $C_9H_{16}O_2N_4S$, has m. p. 135°, and is not readily desulphurised. J. J. S.

Purines. II. An Isomeride of Xanthine; 2 : 8-Dioxypurine. Carl O. Johns (*Amer. Chem. J.*, 1911, **45**, 79—87).—In an earlier paper (Abstr., 1909, i, 192) an account was given of 2 : 8-dioxy-6-methylpurine, which was prepared by the condensation of 5 : 6-diamino-2 : 4-methylpyrimidone with carbamide. 2 : 8-Dioxypurine has now been obtained in a similar manner.

2 : 8-*Dioxypurine* (annexed formulæ), obtained in a yield of 92% of the theoretical by heating a mixture of 5 : 6-diamino-2-pyrimidone (Johnson, Johns, and Heyl, Abstr., 1906, i, 771) and carbamide at 180—190°, resembles xanthine (2 : 6-dioxypurine) in many respects, and gives the murexide reaction. If carbon dioxide is passed into a solution of the substance in potassium hydroxide, or if a solution in a mineral acid is poured into water, the free base is precipitated. 2 : 8-Dioxypurine can be distinguished from xanthine by means of its *sodium* salt, which forms stout prisms containing $4H_2O$. The *hydrochloride*, *dinitrate*, and *ammonium* and *potassium* salts are also described; the last-mentioned crystallises with $2H_2O$.



5 : 6-Diamino-2-pyrimidone can be obtained in a yield of 65% of the theoretical by reducing 5-nitrocytosine with ferrous hydroxide; its *hydrochloride*, $C_4H_6ON_4,2HCl$, *sulphate*, $C_4H_6ON_4,H_2SO_4,H_2O$, and *nitrate*, $C_4H_6ON_4,4HNO_3$, are described. When this compound is heated with sulphuric acid of 20% strength in a sealed tube at 140—150°, it is converted into *iso*barbituric acid. E. G.

Quadriurates. RUDOLF KOHLER (*Zeitsch. physiol. Chem.*, 1911, 70, 360—387).—Attempts were made to prepare the quadriurates first described by Bence Jones (this Journ., 1862, 15, 201) by mixing saturated sodium biurate solution with a primary phosphate, and by introducing uric acid into hot acetate solutions of varying concentration. The salts were also sought for in snake excrement. The salts have not the composition $H_2C_5H_2O_3N_4,MHC_5H_2O_3N_4$ attributed to them by Bence Jones, but appear to be a mixture of primary urate and uric acid in the proportion of 1 : 1. By varying the concentration of the acetate solution, mixtures varying in concentration to biurate may be obtained. It is shown that this is in agreement with theoretical considerations.

The hydrolysis by water is not characteristic of the so-called quadriurates, as some do not show it at all, whereas some biurates are hydrolysed. It is due to the partial absorption of acid during the formation of the salt: this passes out into water and causes decomposition. The same reasoning applies to the decomposition of snake excrement by water, and to simultaneous precipitation of biurate and uric acid from human urine, as witnessed by the decrease in acidity after the formation of sediment. E. F. A.

Action of Azoimide on the Carbylamines. E. OLIVERI-MANDALÀ and B. ALAGNA (*Gazzetta*, 1910, 40, ii, 441—444. Compare Abstr., 1910, i, 343).—By the action of azoimide on the corresponding carbylamines, other homologous tetrazoles can be prepared in the manner already described for 1-methyltetrazole. 1-*Ethyltetrazole*, $C_3H_6N_4$, is a liquid, b. p. 155—156° 14 mm.; it forms a stable *platinichloride*, $(C_3H_6N_4)_2PtCl_4$. 1-Phenyltetrazole (compare Freund and Paradies, Abstr., 1901, i, 770) has m. p. 65—66°. R. V. S.

The Course of the Sandmeyer Reaction. GUSTAV HELLER and WALTER TISCHNER (*Ber.*, 1911, 44, 250—255. Compare Abstr., 1910, i, 240).—The authors have investigated the velocity of decomposition of benzenediazonium chloride, and also of *o*- and *p*-toluenediazonium chlorides, in aqueous hydrochloric acid solution in the presence of cuprous chloride by measuring the rate of evolution of nitrogen.

It is found that the velocity depends not only on the temperature and concentration both of the acid and of the diazonium compound, but also to a great extent on the nature of the diazonium compound itself, slight changes in the constitution producing considerable differences in the course of the decomposition; catalytic influences also play a considerable part in determining the rate of decomposition.

In the case of benzenediazonium chloride, free nitrous acid and also excess of cuprous chloride influence the decomposition in a marked, but irregular, manner. With *p*-toluenediazonium chloride, the velocity at the beginning of the reaction is very small, and then gradually increases; this increase is followed by a gradual diminution in the rate of decomposition, and, finally, by a rapid rise to a maximum, when the reaction quickly comes to an end.

In the case of *o*-toluenediazonium chloride, the rate of decomposition is very slow at first, then rises rapidly to a maximum in about two hours, and slowly diminishes. F. B.

o-Arylazo-compounds of Heterocyclic Phenols: 3-Methyl-4-arylazo-5-hydroxy*iso*oxazole. CARL BÜLOW and ARNULF HEGKING (*Ber.*, 1911, **44**, 238—250).—Knorr and Reuter's 4-benzeneazo-5-hydroxy-3-methyl*iso*oxazole, $\begin{matrix}O\cdot C(OH)\\ \|\\ N{:}CMe\end{matrix}\!\!>\!C\cdot N{:}NPh$ (Abstr., 1891, i, 371; compare Schiff, Abstr., 1896, i, 83), can be readily prepared by the addition of an aqueous solution of sodium acetate and hydroxylamine hydrochloride to a boiling alcoholic solution of ethyl benzeneazoacetoacetate. It dissolves in alkalis, and is reprecipitated by carbon dioxide. The *silver* salt, $C_{10}H_8O_2N_3Ag$, when slowly heated, has m. p. 208—210° (decomp.). The sodium salt, $C_{10}H_{18}O_2N_3Na.H_2O$, was prepared by Schiff and Viciani (Abstr., 1897, i, 444), who considered it to be sodium β-oximino-α-phenylhydrazonoacetoacetate,

$$HO\cdot N{:}CMe\cdot C(N\cdot NHPh)\cdot CO_2Na.$$

The authors find, however, that this sodium salt loses one molecule of water of crystallisation when kept in a vacuum over sulphuric acid, and is readily hydrolysed with the formation 4-benzeneazo-5-hydroxy-3-methyl*iso*oxazole; when treated with hydrochloric acid, it yields the original heterocyclic phenol (compare Schiff and Viciani, *loc. cit.*).

These facts are in contradiction to the view that the solubility of 4-benzeneazo-5-hydroxy-3-methyl*iso*oxazole in alkalis is due to the rupture of the *iso*oxazole ring with the formation of salts of oximinophenylhydrazonoacetoacetic acid, and support the contention of Bülow and Haas (Abstr., 1910, i, 902) that the products obtained by the action of diazonium salts on 3-substituted *iso*oxazolones are azo-derivatives of heterocyclic phenols: $\begin{matrix}O\cdot C(OH)\\ \|\\ N{=}CR\end{matrix}\!\!>\!C\cdot N{:}N\cdot R.$

The *iso*oxazolones themselves are also represented by the hydroxylic and not the ketonic formulæ.

When 4-benzeneazo-5-hydroxy-3-methyl*iso*oxazole is boiled with concentrated potassium hydroxide solution, 2-phenyl-4-methyl-2:1:3-triazole, $\begin{matrix}CMe{:}N\\ \|\\ CH{-}{=}N\end{matrix}\!\!>\!N\cdot Ph$ (von Pechmann, Abstr., 1888, 1287), and α-methylglyoxal-α-oxime-β-phenylhydrazone are produced. The authors consider that the first stage in this reaction consists in the rupture of the *iso*oxazole ring and the formation of

$$NaO\cdot N{:}CMe\cdot C(N_2Ph){:}C(ONa)_2,$$

which then loses sodium carbonate, yielding the oxime-hydrazone, *α-Methylglyoxal-α-oxime-β-phenylhydrazone*,

$$HON{:}CMe\cdot CH{:}N\cdot NHPh,$$

forms yellow crystals, m. p. 147—148°, which become yellowish-brown on keeping; it reduces silver nitrate and Fehling's solutions, and gives an intense reddish-violet coloration when its solution in concentrated sulphuric acid is treated with ferric chloride or potassium dichromate. When heated with phenylhydrazine, it is converted into

methylglyoxalosazone, NHPh·N:CMe·CH:N·NHPh (von Pechmann, Abstr., 1887, 1103).

4-p-*Nitrobenzeneazo-5-hydroxy-3-methylisooxazole*, $C_{10}H_8O_4N_4$, is prepared by the interaction of equal molecular quantities of nitric acid and 4-benzeneazo-5-hydroxy-3-methylisooxazole in concentrated sulphuric acid solution; it forms felted needles, m. p. 176—177°, dissolves in strong sulphuric acid with a greenish-yellow colour, and does not give the Bülow reaction for hydrazones.

4-*Dinitrobenzeneazo-5-hydroxy-3-methylisooxazole*, $C_{10}H_7O_6N_5$, prepared in a similar manner from two mols. of nitric acid, crystallises in yellow leaflets, m. p. 184—185°.

4-o-*Toluencazo-5-hydroxy-3-methylisooxazole*, $C_{11}H_{11}O_3N_3$, is prepared by the gradual addition of an aqueous solution of hydroxylamine and sodium acetate to a boiling alcoholic solution of ethyl o-toluenecazoacetoacetate; it has m. p. 154—155°, and dissolves in alkalis with a yellow colour.

4-p-Toluenecazo-5-hydroxy-3-methylisooxazole, $C_{11}H_{11}O_3N_3$, obtained in a similar manner from ethyl p-toluenecazoacetoacetate, crystallises in yellow needles, m. p. 203°(Schiff: 202°).

4-m-*Xylenecazo-5-hydroxy-3-methylisooxazole*, $C_{12}H_{13}O_3N_3$, forms orange-yellow needles, m. p. 124—125°; its salts with alkalis are decomposed by carbon dioxide.

4-α-Naphthalenecazo-5-hydroxy-3-methylisooxazole, $C_{14}H_{11}O_3N_3$, crystallises in brick-red leaflets, m. p. 172—173° (Schiff: 168—170°), and dissolves in concentrated sulphuric acid with a deep bluish-red colour.

4-β-*Naphthalenecazo-5-hydroxy-3-methylisooxazole*, $C_{14}H_{11}O_3N_3$, forms stout, brownish-yellow needles, m. p. 201—202°; its solutions in strong sulphuric acid have a reddish-orange colour.

By the interaction of sodium acetate, hydroxylamine hydrochloride and ethyl o-carboxybenzeneazoacetoacetate in alcoholic solution, *ethyl α-o-carboxybenzeneazo-β-oximinoacetoacetate*,

$$HON{:}CMe{\cdot}CH(N_2{\cdot}C_6H_4{\cdot}CO_2H){\cdot}CO_2Et,$$

is produced. The latter compound has m. p. 207—208°, and yields 4-o-*carboxybenzeneazo-5-hydroxy-3-methylisooxazole*, $C_{11}H_9O_4N_3$, yellow leaflets, m. p. 232°, when boiled in glacial acetic acid solution.

Ethyl nitrocarboxybenzeneazoacetoacetate, $C_{13}H_{13}O_7N_3$, obtained by nitrating ethyl carboxybenzeneazoacetoacetate, crystallises in felted, yellow needles, m. p. 188—189°; the *oxime*, $C_{13}H_{14}O_7N_4$, has m. p. 222°, and could not be converted into the corresponding *isooxazolone*.

F. B.

The State of Aggregation of Matter. I—III. Samuel B. Schryver (*Proc. Roy. Soc.*, 1910, *B*, 83, 96—123).—I. *Action of Salts in Heterogeneous Systems and the Nature of the Globulins.*—When formaldehyde acts on a solution of Witte's peptone, a precipitate is formed. This precipitation can, however, as Sollman has shown, be inhibited by the presence of salts. The titration of the mixture by alkali, even in the absence of precipitate formation, shows that the formaldehyde has acted on the amino-groups with the formation of methyleneimino-peptones. The inhibitory action of salts on pre-

cipitate formation can, however, be explained if the methyleneimino-peptones undergo polymerisation or condensation to form more complex molecules, and behave in the same way as methylenesparagine behaves, according to the investigations of Schiff. If the unpolymerised or uncondensed methyleneimino-peptones are of such complexity as to form colloidal solutions, they can adsorb salt molecules from solution, which sterically inhibit their reactions with one another and prevent the formation of the insoluble complexes. A quantitative investigation of the inhibitory action of a large number of salt solutions showed that (with certain explicable exceptions), those which possessed the greatest power in this respect were the best solvents of the globulins. This suggested an explanation of the nature of these substances which are soluble in salt solution, but insoluble in water. The author gives reasons for supposing that the undissolved globulins are aggregates formed by the combination of a carboxyl group in one molecule with an amino-group in another, by means of which a salt is formed which undergoes a slight, but definite, hydrolysis in the presence of water. Owing to adsorptions of salt, the dissociated globulin molecules are sterically inhibited from reaggregation; the more readily a salt is adsorbed, the greater the solvent or (diaggregeting) capacity as regards the globulin. The results indicate that owing to their adsorption capacities, chemical reactions of colloids do not follow the ordinary laws of mass action. The solvent capacity of salts for globulins can be correlated with two physical properties of their aqueous solutions, namely, their surface tensions and their viscosities: the higher the surface tension and the viscosity of a salt, the smaller its solvent capacity for the globulins. The influence of the former property can be deduced from a general study of adsorption phenomena, and of the latter by an extension of Noyes and Whitney's and of Nernst's generalisations on the rate of action in heterogeneous systems, with the assumption of the existence of a diffusion layer at the limiting surfaces. Salts also exert similar action in systems other than those containing proteins. Thus, the critical solution temperature of phenol and salt solutions is shown to be a function of the surface tension of the latter. Furthermore, the solubility of certain crystalline substances in salt solutions, especially of amphoteric substances, is shown to follow similar laws to the globulins. The surface tensions and viscosities of a series of salt solutions, together with the solubility of edestin and serum-globulin in these solutions, are tabulated.

II. *Action of Formaldehyde on Witte's Peptone.*—It is shown that the precipitate is formed from the more complex constituents of the peptones. Owing to the acidic nature of the methyleneimino-peptones, the salts of the weaker acids exert a greater inhibitory capacity on precipitate formation than would be deduced from their surface tensions and viscosities, as double decomposition can take place.

III. *The Solubility of Phenol and Certain Crystalline Substances in Salt Solutions.*—The solubilities of *dl*-leucine, *dl*-phenylalanine, caffeine, benzamide, and *p*-toluidine in the series of salt solutions employed in the investigations on the globulins are tabulated.

S. B. S.

Organic Colloids. S. J. Levites (*Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 4—8).—Observations are recorded in reference to the solubility and precipitability of proteins and the adsorption of tannin by gelatin.

Glutin is readily soluble in solutions of iodides and thiocyanates; casein in solutions of potassium iodide, sodium thiocyanate, potassium nitrate, and sodium phosphate. Aqueous pyridine is a good solvent for various proteins. Glutin and casein are both insoluble in water and in anhydrous pyridine, but dissolve in water-pyridine mixtures, the maximum solubility corresponding with a solvent of the composition $C_5H_5N + 2H_2O$. Glutin and Witte's peptone are readily soluble in formamide, and the solutions can be diluted with water without precipitation. The formamide and aqueous pyridine solutions of the proteins are very viscous.

In regard to the precipitation of proteins, it has been found that Witte's peptone and gelatin are precipitated by cadmium iodide in very dilute solution. Solutions of zinc and cadmium sulphates only give rise to a slight opalescence when added to Witte's peptone, and have no effect on a gelatin solution.

From experiments on the adsorption of tannin by gelatin from tannin solutions of different concentrations, it has been found that the proportion of adsorbed substance diminishes as the concentration increases. For a given solution the adsorption increases with the period of swelling of the gelatin. In presence of an electrolyte (potassium aluminium sulphate), the adsorption of tannin by gelatin is diminished, and the influence of the concentration of the tannin solution on the magnitude of the adsorption is very greatly reduced.

H. M. D.

Methylation of Gelatin. Zdenko H. Skraup and B. Böttcher (*Monatsh.*, 1910, **31**, 1035—1050).—The authors find that gelatin contains a small quantity of methyl in the form of the groups ·OMe and :NMe, and that the percentage of methyl, in both forms, increases on methylation.

When hydrolysed, the methyl derivative yields histidine and arginine in quantities amounting to 10% of those furnished by gelatin itself, traces of glutamic acid, and no lysine; leucine, alanine, glycine, pyrrolidinecarboxylic acid, and phenylalanine were also found amongst the products of hydrolysis. The hexone bases and glutamic acid are thus destroyed on methylation, whereas the leucine, alanine, etc., remain unchanged.

Comparing these results with those obtained in the case of casein (Abstr., 1909, i, 748), the authors draw the conclusion that the arrangement of the glutamic acid residue in the latter compound is different from that in gelatin.

Methylgelatin, prepared by boiling a solution of gelatin in alcoholic potassium hydroxide with methyl iodide, forms an amorphous, yellow mass, which, when powdered, is almost white: it is soluble in water, and is precipitated on the addition of ammonium sulphate. The xantho-protein reaction is more marked than with ordinary gelatin. F. B.

The Pepsin-chymosin Question. J. F. B. VAN HASSELT (*Zeitsch. physiol. Chem.*, 1910, 70, 171—185).—The experiments quoted bear against the view that pepsin and rennin (chymosin) are one and the same substance. It is possible to obtain preparations which exhibit only one action; anti-substances also inhibit differently the two enzymatic actions. W. D. H.

Diastase and Commercial Lecithin Preparations. HERMAN LAPIDUS (*Biochem. Zeitsch.*, 1910, 30, 39—55). The amount of action was determined by estimating the reducing sugars formed (calculated as maltose, for which the author has worked out tables). Wohlgemuth's iodine method was not available, owing to the action of this substance on the lecithin. The lecithin inhibits the action of ptyalin to a marked extent, but not to a relatively greater extent when small amounts of saliva are employed as compared with its inhibitory action on larger amounts of saliva. There does not appear, therefore, to be any evidence of combination between saliva and lecithin. The inhibitory influence is more marked at room temperature than at body temperature. The action of lecithin on pancreas diastase is similar, although here there is not such a marked difference between the action at room temperature and body temperature. With serum diastase, the results obtained are somewhat complicated, as the amount of diastase in the serum alters (increases) with age and diminishes after extraction with ether. The lecithin in this case diminishes the action at room temperature; at body temperature it sometimes increases and sometimes diminishes the action. Generally the action is weakly inhibitory. If, however, the serum which has been extracted with ether is employed, lecithin markedly increases the diastatic action. The above experiments were carried out with ox-serum. In human serum (from placenta) the diastatic action was weak, but was increased by addition of lecithin. Similar results were obtained with syphilitic sera, in which the diastatic action is stronger than in the normal.

S. B. S.

Hæmoglobin as a Peroxydase. GABRIEL BERTRAND and FELIX ROGOSINSKI (*Compt. rend.*, 1911, 152, 148—151; *Bull. Soc. chim.*, 1911, [iv], 9, 149—152. Compare Wolff and Stoecklin, Abstr., 1910, i, 802).—The peroxydase character of oxyhæmoglobin is also shared by carboxyhæmoglobin and cyanohæmoglobin; it appears, therefore, not to be due to the ability of oxyhæmoglobin to part with oxygen, but to depend on the presence of iron in the molecule. W. O. W.

Extraction of Zymase by Simple Maceration. A. VON LEBEDEFF (*Compt. rend.*, 1911, 152, 49—51).—It is not necessary to employ Buchner's method to obtain a preparation of zymase from yeast. The solution obtained by macerating one part of dried yeast with 2·5—3 parts of water, on filtering through paper after being allowed to remain overnight, has greater activity and stability than that prepared by the usual method. W. O. W.